COMPARISON OF NICKEL MOLYBDENUM HYDROUS METAL OXIDES WITH COMMERCIAL CATALYSTS FOR HDS/HDN OF COAL LIQUIDS

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INTRODUCTION

Improved efficiency in direct coal liquefaction processes can be obtained by developing catalysts with better activity, selectivity, and life. In previous exploratory research at Sandia National Laboratories, catalysts prepared via hydrous metal oxide (HMO) ion exchangers have been shown to have potential for application to a number of reactions associated with the conversion of coal to liquid fuels.[1] In the present effort, one member of this class of catalysts, hydrous titanium oxide (HTO), has been used to develop catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of coal liquids.

EXPERIMENTAL

Synthesis

The HTO catalysts have been prepared in both a bulk form and a thin-film variation. Specifics on preparation of the HTOs are found elsewhere.[2] Briefly, tetra-ethyl orthosilicate and tetra-isopropyl titanate were combined in a 1:5 molar ratio with NaOH and excess methanol. The soluble intermediate resulting from this reaction was either coated onto a support or precipitated from solution with an acetone/water wash. The catalyst was acidified followed by ion-exchanging with ammonium molybdate. Nickel in a nitrate form was applied by incipient wetness.

Batch Testing

For batch model compound screening studies, the bulk (unsupported) catalysts were pelletized, crushed to 30/40 mesh, calcined at 500°C for 1 hour, sulfided at 420°C for 2 hours in 10% H_2S/H_2, ground to -200 mesh, and evaluated. The supported catalysts were calcined and sulfided in the extrudate form, ground to -200 mesh, and evaluated. Batch model compound hydrogenation studies were conducted with pyrene. Pyrene (100 mg), hexadecane (1 g), and catalyst (10 mg) were loaded into a microautoclave reactor that was pressurized to 500 psig with hydrogen. Reaction conditions were 300°C for 10 minutes.

Continuous Testing

For studies involving continuous testing, a subbituminous coal derived liquid feed was obtained from HRI's catalytic two-stage PDU. The reactor was loaded with 10 grams of catalyst mixed with 10 grams of α-alumina diluent, which was placed in the center of either a 7/16" or 3/4" I.D. stainless steel tube. Approximately 2" of α-alumina was placed above, and below the 30/40 mesh catalyst bed as pre-heat and post-heat zones. All catalysts were sulfided *insitu* with a 10% H_2S/90% H_2 gas mixture at 100 sccm for 4 hours at 400°C. The coal derived liquid, fed at 0.45 cc/min, had a composition of ca. 500 ppm sulfur and 1400 ppm nitrogen. Typical experiments lasted 4 to 5 days and were run at 400°C and at either 500, 1000, or 1500 psig hydrogen. Coal liquid samples were pulled 4 to 5 times a day and analyzed for sulfur and nitrogen content using an Antek 7000 S/N analyzer. Activities are reported as percent sulfur/nitrogen removed from the feed. A few coal liquid samples were characterized by proton NMR using a technique developed by CONSOL[3] to evaluate hydrogen distribution. In addition, the feed was further characterized by separating the material into paraffins and aromatics over acidic alumina.

RESULTS AND DISCUSSION

Feed and Product Characterization

[1] Sandia Technical Report, SAND89-2400, Sandia National Laboratories, Albuquerque, NM (1990)
[2] Sandia Technical Report, SAND89-2399, Sandia National Laboratories, Albuquerque, NM (1990)
[3] R. A. Winschel, G.A. Robbins, F.P. Burke, *Fuel*, **65**, pp 526-532 (1986)

Proton NMR spectra for the feed were compared to proton NMR spectra for product samples from two different catalyst runs: 500 psig and 1000 psig with nickel molybdenum hydrous metal oxide (NiMoHTO) on an Amocat 1C blank. These spectra indicated that little change in hydrogen character occurred at either condition. To further quantify the feed, the non-paraffinic portion of the feed was extracted over a column of acidic alumina. The effluent oil from the alumina column was compared to the feed oil by gas chromatography and results indicated that the feed was of a highly paraffinic nature. Due to the high paraffin content of the feed, it was reasonable that minimal boiling point upgrading occurred. These experiments indicated that the coal derived oil selected was an appropriate feed material, in that the HDS/HDN reactions would not be in competition for feed hydrogen with bond saturation reactions.

Batch Testing - Hydrogenation (HYD) of Pyrene.
The results for the pyrene HYD experiments are shown in Figure 1. The first order HYD activities are calculated on both a catalyst weight basis and on a weight of total active metals basis, *i.e.* molybdenum and nickel. The activity of the bulk (unsupported) NiMoHTO (8.5%Mo/2.9%Ni) was higher than either Shell 324 (13%Mo/2.7%Ni) or Amocat (10.7%Mo/2.4%Ni) on either basis. When comparing the activities for the supported NiMoHTO catalysts with their commercial counterparts, the NiMoHTO catalysts had higher activities. For the NiMoHTO on the Shell support (8.8%Mo/2.9%Ni), the NiMoHTO was 12% more active on a catalyst weight basis and 81% more active on an active metals basis. The results for the NiMoHTO on the Amocat support (9.2%Mo/3.0%Ni) compared to the Amocat 1C catalyst were similar: 25% more active on a catalyst weight basis and 52% more active on a metals basis. The higher activities of the NiMoHTO catalysts as compared to the commercial catalysts, especially on an active metals basis, is due in part to the high dispersion of the MoS_2 on the HTO. TEM studies have indicated that the MoS_2 dispersion is higher on a NiMoHTO catalyst as compared to a commercial catalyst. A second explanation for the higher activity is the higher acidity of the NiMoHTO as compared to commercial catalysts supported on alumina. The catalyst acidity was measured by ammonia adsorption. In terms of moles of ammonia per gram of catalyst, the bulk NiMoHTO adsorbed 43% more ammonia than Shell 324. The higher acidity of the NiMoHTO may lead to a higher HYD activity for the HTO catalysts.

Flow Reactor Testing - HDS and HDN of Coal Liquids.
The HDS/HDN activity in terms of total removed sulfur and nitrogen was measured at 500, 1000, and 1500 psig for unsupported (bulk) NiMoHTO, Shell 324, Amocat 1C, and NiMoHTO catalysts supported on Shell and Amocat blanks. The bulk and supported NiMoHTO catalysts had a lower total active metals concentration than either Shell 324 or Amocat 1C. The following results are presented as a percentage sulfur or nitrogen removed at a constant reactor space velocity (SV). The SV was based on total catalyst weight and not on active metals. If the results were based on total active metals, the activity of the NiMoHTO catalysts would be higher. In general, the estimated error in the HDS and HDN activities was estimated to be ±1-2%. In the interest of publication space, only the HDS results are shown in Figures 2-7.

(i) 500 psig The HDS activities of the evaluated catalysts are shown in Figures 2 and 3. At 500 psig, the bulk NiMoHTO activity (9.7%Mo/3.2%Ni) was higher than either Shell 324 or Amocat 1C. The bulk NiMoHTO catalyst had a higher activity than Amocat 1C with a lower loading of active metals. Since the NiMoHTO catalysts have a higher dispersion of MoS_2 than standard commercial catalysts[1], it is not unexpected that HDS activities can be maintained with a lower NiMo composition. At 500 psig, the bulk NiMoHTO was significantly more active for HDS than Shell 324 (Figure 3).

The trends for the HDN activities were similar to the HDS activities. After 80 hours on-line, the HDN activity for the bulk NiMoHTO was about 21%. This was significantly higher than the 80 hour HDN activities of Shell 324, Amocat 1C, and NiMoHTO on an Amocat blank: 13%, 9%, and 15% respectively. In general at 500 psig, the bulk NiMoHTO outperformed, and the supported NiMoHTO catalysts achieved near equal performance to the commercial catalysts for HDS and HDN activities while containing less active metals.

(ii) 1000 psig The HDS activities for the bulk NiMoHTO (9.6%Mo/3.2%Ni), Amocat supported NiMoHTO (8.1%Mo/2.7%Ni) and Amocat 1C catalysts are shown in Figure 4. Line-out HDS activities were between 86% and 90% for all three catalysts with the

Amocat 1C activity being slightly higher than either of the NiMoHTO catalysts. Figure 5 shows the data for the bulk NiMoHTO, Shell 324, and Shell supported NiMoHTO (8.9%Mo/2.9%Ni) catalysts. The HDS activity of the Shell 324 was higher than either the Shell supported NiMoHTO or the bulk NiMoHTO catalysts by about 3%.

The 80 hour HDN performance for the five catalysts in Figures 4 and 5 were ranked as follows; Shell 324 (45%), bulk NiMoHTO (43%), Amocat 1C (42%), Amocat supported NiMoHTO (42%), and Shell supported NiMoHTO (39%). Given an estimated error of ±2%, minimal differences were found in performance on a total catalyst weight basis, although the supported NiMoHTO catalysts contained 18% and 25% less active metals as compared to Amocat 1C and Shell 324 respectively.

(iii) 1500 psig The HDS activity for the bulk NiMoHTO (9.6%Mo/3.2%Ni), Amocat supported NiMoHTO (7.8%Mo/2.6%Ni) and Amocat 1C catalysts are shown in Figure 6. The bulk NiMoHTO and Amocat 1C catalysts performed slightly better than the Amocat supported NiMoHTO. The Shell 324, Shell supported NiMoHTO, and the bulk NiMoHTO performed similarly (Figure 7). The HDN activities for the Bulk NiMoHTO, Shell 324 and Shell supported NiMoHTO all performed similarly; about 64±2%. The results for the Amocat 1C and Amocat supported NiMoHTO were significantly less: about 55%.

CONCLUSIONS
For HYD of pyrene, unsupported NiMoHTO catalysts performed better than commercial benchmark catalysts on either a catalyst weight or active metals basis. In a side-by-side comparison of supported NiMoHTO catalysts with commercial counterparts, the supported NiMoHTO catalysts outperformed the Shell 324 and Amocat 1C catalysts for HYD of pyrene. For HDS/HDN of coal liquids, the supported and bulk forms of the NiMoHTO catalysts equaled the performance of the commercial catalysts at 500, 1000, and 1500 psig while containing less active metals. Possible reasons for the high activity of the NiMoHTO catalysts are a high dispersion of the active MoS_2 phase and a high acidity of the bulk NiMoHTO.
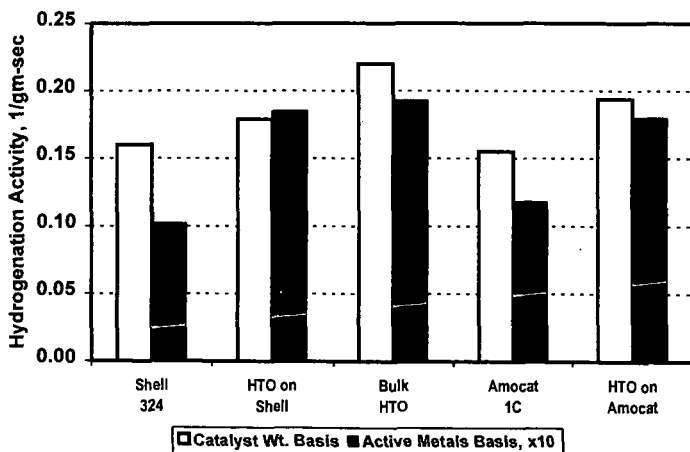
Figure 1. HYD Pyrene Activity of Commercial and Hydrous Metal Oxide Catalysts
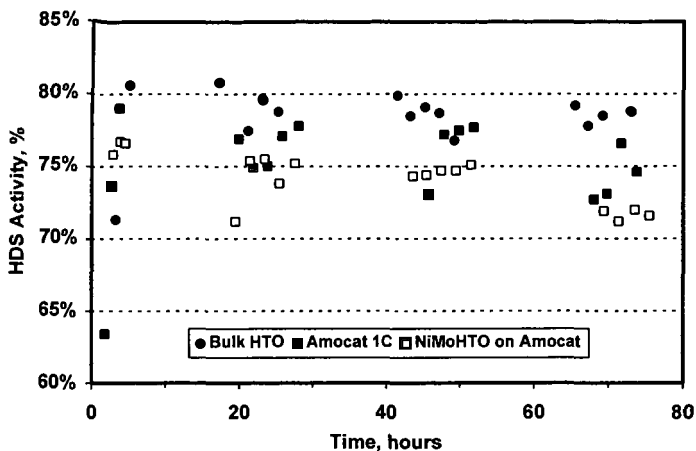
Figure 2. 500 psig HDS Activity of Benchmark and HTO Catalysts
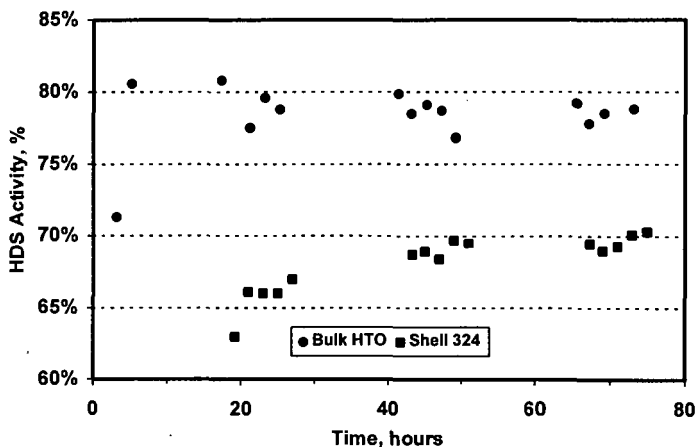*(note change in scale)*

Figure 3. 500 psig HDS Activity of Benchmark and HTO Catalysts
(note change in scale)

Figure 4. 1000 psig HDS Activity of Benchmark and HTO Catalysts
(note change in scale)

Figure 5. 1000 psig HDS Activity of Benchmark and HTO Catalysts
(note change in scale)

Figure 6. 1500 psig HDS Activity of Benchmark and HTO Catalysts
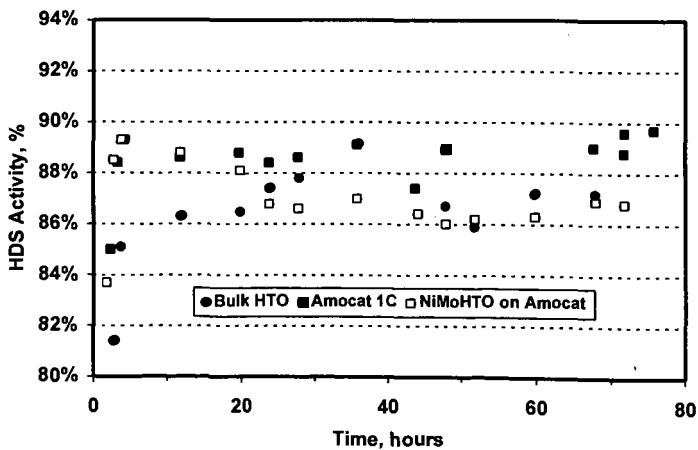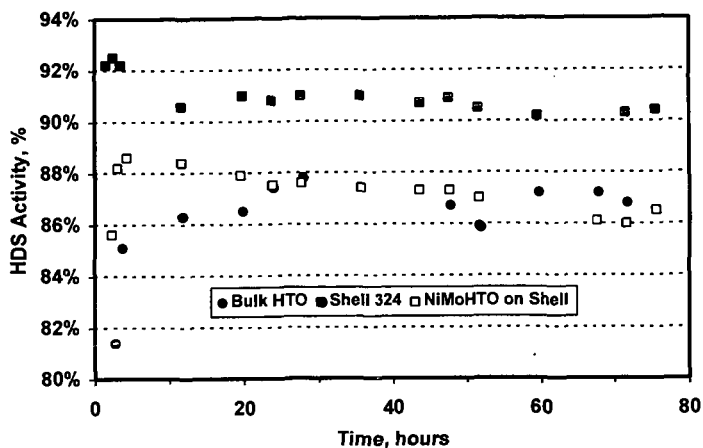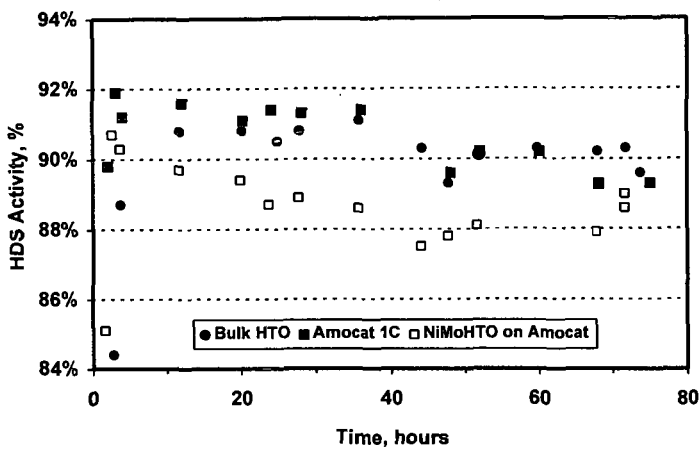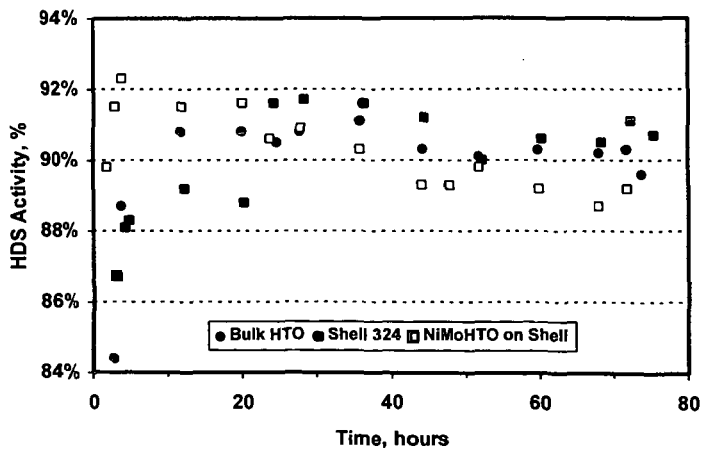*(note change in scale)*

Figure 7. 1500 psig HDS Activity of Benchmark and HTO Catalysts
(note change in scale)

CHARACTERIZATION OF SILICA-DOPED HYDROUS TITANIUM OXIDE (HTO:Si)-SUPPORTED NICKEL MOLYBDENUM (NiMo) CATALYST COATINGS

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Keywords: hydrous titanium oxide, ion exchange, Mo

INTRODUCTION
Hydrous Metal Oxides (HMOs) are chemically synthesized materials which contain a homogeneous distribution of ion exchangeable alkali cations that provide charge compensation to the metal-oxygen framework. Both the presence of these alkali cations and the resulting high cation exchange capacities (4-5 meq/g) clearly set these HMO materials apart from conventional precipitated hydrous oxides.[1,2] For catalyst applications, the HMO material serves as an ion exchangeable support which facilitates the uniform incorporation of catalyst precursor species. Following catalyst precursor incorporation, an activation step is required to convert the catalyst precursor to the desired active phase.

Considerable process development activities at Sandia National Laboratories related to HMO materials have resulted in bulk silica-doped hydrous titanium oxide (HTO:Si)-supported NiMo catalysts that are more active in model reactions which simulate direct coal liquefaction (e.g., pyrene hydrogenation) than commercial NiMo catalysts. However, extension of this process to produce NiMo/HTO:Si catalyst coatings on commercial supports is of interest for liquefaction applications since overall catalyst cost can be reduced and bulk HTO:Si mechanical limitations can be circumvented. This paper will describe how the bulk NiMo/HTO:Si catalyst preparation process was extended to fabricate catalyst coatings on engineered supports. Initial efforts related to the catalyst coating procedures and the characterization of the Mo ion exchange/adsorption procedure will be discussed. The Mo ion exchange/adsorption process is complicated in the case of the catalyst coatings due to the presence of two potential Mo adsorption sites (i.e., HTO:Si film vs. commercial support). These results will be correlated with pyrene hydrogenation reactivity and catalyst coating microstructure.
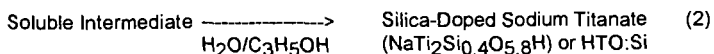
EXPERIMENTAL PROCEDURE
HMO-supported catalyst preparation involves a multiple step chemical procedure which begins with the synthesis of a bulk HMO powder or HMO coating. This chemistry, which can be utilized to produce alkali titanates, alkali zirconates, alkali niobates, or alkali tantalates, has been described in detail elsewhere.[3-5] Previous work has demonstrated that SiO_2 additions (Ti:Si molar ratio $= 5:1$) to HMO materials act to stabilize HMO support surface area at high temperature ($\geq 500°C$) without significantly altering ion exchange properties.[4,5] A brief review of the synthesis of silica-doped sodium titanate (HTO:Si) with a maximum ion exchange capacity (Na:Ti mole ratio = 0.5) will be given here as an example. The first step of the reaction scheme involves the addition of a mixture of tetraethoxysilane and titanium isopropoxide to a dilute (~10 wt.%) solution of sodium hydroxide in methanol, resulting in the production of a soluble intermediate species as follows:

$$Ti(OC_3H_7)_4 + 0.2\ Si(OC_2H_5)_4 + 0.5\ NaOH \xrightarrow[\text{CH}_3\text{OH}]{} \text{Soluble Intermediate (1)}$$
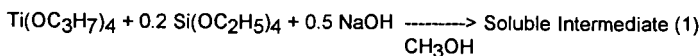
The exact chemistry involved in the formation and subsequent reaction of the soluble intermediate species is extremely complex. Possible competing reactions include exchange of methoxide groups for isopropoxide groups coordinated to Ti, precipitation and redissolution of titanium methoxide, partial hydrolysis or condensation of the various Si, Ti, or mixed alkoxide species, and sodium methoxide formation. Structural studies are in progress to better characterize the nature of the soluble intermediate species.

To prepare bulk HTO:Si powders, the soluble intermediate is subsequently hydrolyzed in a mixed water/acetone solution to produce the silica-doped sodium titanate as follows:

$$\text{Soluble Intermediate} \xrightarrow[\text{H}_2\text{O/C}_3\text{H}_5\text{OH}]{} \quad \begin{array}{c}\text{Silica-Doped Sodium Titanate} \\ (\text{NaTi}_2\text{Si}_{0.4}\text{O}_{5.8}\text{H}) \text{ or HTO:Si}\end{array} \quad (2)$$

The chemical formula in equation (2) assumes uniform incorporation of all reactants; this has been confirmed by various chemical analyses. The amorphous HTO:Si precipitate is filtered, washed, and vacuum dried at room temperature to produce the material for subsequent ion exchange (IE) processing.

As an alternative to bulk HTO:Si preparation, HTO:Si coatings can be prepared by exposing the soluble intermediate from equation (1) to other materials with a pre-engineered shape (e.g., monoliths, spheres, extrudates, etc.). Depending on the porosity and surface chemistry of the pre-engineered shape, dilution of the soluble intermediate, the coating technique, and the drying conditions, thin or thick film HTO:Si coatings can be fabricated.[4,5] This paper will focus on thick film catalyst coatings on γ-Al$_2$O$_3$ extrudate (Amocat 1C alumina blanks, 1/12 in. dia, 8879-85-C), and the resulting NiMo catalysts, although many other pre-engineered materials, shapes, and catalysts have been evaluated. These coatings were prepared by soaking the as-received γ-Al$_2$O$_3$ extrudate in an undiluted soluble intermediate solution for 24 h, followed by vacuum filtration, and room temperature vacuum drying.

With the exception of the Amocat 1C catalyst , which was commercially prepared by an incipient wetness technique, similar Ni and Mo loading techniques were used for all other catalysts. Following the fabrication of the bulk HTO:Si powder or HTO:Si coated γ-Al$_2$O$_3$ extrudate, these materials were initially acidified with HCl to pH 2.5 or 4.0 (for coated vs. bulk catalysts, respectively) to remove Na, washed with deionized H$_2$O, and vacuum dried. Following this procedure, Mo anion exchange/adsorption was performed over a 30 min or 24 h period (for bulk vs. coated catalysts, respectively) in an aqueous solution (0.02-0.07 M) of ammonium heptamolybdate (AHM), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, at an initial pH of 3.5-3.9. Nominal targeted Mo loading for both the bulk HTO:Si powder and the HTO:Si coated γ-Al$_2$O$_3$ catalysts was ~10 wt.%. The Mo precursor loaded materials were vacuum filtered, rinsed with deionized H$_2$O and acetone, and subsequently dried under vacuum at room temperature. After chemical analysis for Mo by atomic absorption spectrophotometry, Ni was added to the Mo precursor loaded materials via incipient wetness using Ni(NO$_3$)$_2$·6H$_2$O, followed by overnight drying in ambient air at room temperature and oven drying in air at 100°C for 2 h. Regardless of the Mo loading level in the catalyst, a constant ratio of moles Ni/(moles Ni + moles Mo) = 0.35 was used to determine the Ni loading for each batch. The final catalyst precursor was activated by first calcining in air at 500°C for 1 h and then sulfiding in 10% H$_2$S in H$_2$ at 420°C for 2 h. Bulk catalysts were pelletized and granulated to -10/+20 mesh prior to activation, while coated catalysts were activated in extrudate form. Following activation, all catalysts were granulated to -200 mesh and evaluated for reactivity using pyrene hydrogenation as a model reaction. Pyrene (0.1 g), hexadecane (1 g), and catalyst (0.010 g) were loaded into a batch microautoclave reactor and tested at 300°C under 500 psig H$_2$ for 10 min.

In addition to fabricating standard bulk NiMo/HTO:Si catalysts, which contain nominally 8-10 wt.% Mo and 2.5-3.5 wt.% Ni, several other catalysts were made in an attempt to simulate the potential extremes involved in the Mo loading of NiMo/HTO:Si coated γ-Al$_2$O$_3$ extrudate. Because of the presence of at least two competing Mo anion adsorption sites, one for the HTO:Si film surface and one for the γ-Al$_2$O$_3$ extrudate surface, it is important to determine the partitioning of Mo between these potential sites and the effect of this partitioning on catalyst reactivity. These two extremes were simulated by performing similar acidification and Mo exchange procedures on the γ-Al$_2$O$_3$ extrudate only and on bulk HTO:Si powder. The quantities of γ-Al$_2$O$_3$ extrudate and bulk HTO:Si powder exposed to the AHM solution were determined by estimating the weight fractions of the HTO:Si coating and the γ-Al$_2$O$_3$ extrudate in the actual HTO:Si coated γ-Al$_2$O$_3$ extrudate. These values, estimated from weight change measurements and separate chemical

analyses, were 20 wt.% HTO:Si coating, and 80 wt.% γ-Al$_2$O$_3$ extrudate. In both the case of the bulk HTO:Si powder and the γ-Al$_2$O$_3$ extrudate, these IE conditions represented approximately a two fold excess of Mo relative to their respective individual Mo adsorption capacities.

RESULTS AND DISCUSSION

The experimental conditions used to prepare these various sulfided NiMo catalysts resulted in a range of Ni and Mo loadings, which are summarized below in Table 1.

Table 1
Catalyst Compositions Resulting from Various Preparation Techniques

Catalyst Description	Wt. % Mo*	Wt. % Ni*
Amocat 1C	10.7	2.4
Bulk NiMo/HTO:Si	9.7	3.2
Blank IE on γ-Al$_2$O$_3$	4.2	1.4
High Mo Bulk NiMo/HTO:Si	14.7	4.8
NiMo/HTO:Si Coated γ-Al$_2$O$_3$	8.5	2.8

* Catalyst weight loadings are expressed on a calcined basis.

For the bulk NiMo/HTO:Si materials, high Mo loadings (> 20 wt.%) are possible due to the high affinity of acidified HTO:Si for anionic Mo species.[3] For our IE conditions, the predominant Mo species in solution should be either $(Mo_7O_{23}OH)^{-5}$ or $(Mo_7O_{24})^{-6}$.[6] Standard bulk NiMo/HTO:Si batches, which contain 8-10 wt.% Mo incorporated via ion exchange/adsorption, are well within the Mo adsorption capacity for these materials. The high affinity of these HTO:Si materials for anionic Mo species is in contrast to oxide supports such as γ-Al$_2$O$_3$ and TiO$_2$, which have reported equilibrium Mo adsorption capacities of < 10 wt.%.[7-9] Consistent with this literature, use of the same IE procedure with the γ-Al$_2$O$_3$ extrudate only (referred to in Table 1 and Figure 1 as Blank IE) results in a lower Mo loading (< 5 wt.%) via ion exchange/adsorption. The fact that the Mo loading is significant, although smaller, on the γ-Al$_2$O$_3$ extrudate, indicates that in the case of the NiMo/HTO:Si coated γ-Al$_2$O$_3$, a competition may exist between ion exchange/adsorption sites on the HTO:Si coating vs. the γ-Al$_2$O$_3$ extrudate surface.

The different Mo loading experiments also revealed potential problems with these IE procedures. In the case of the extrudate samples, exposure to the Mo loading solution over a 24 h period resulted in a fine white precipitate which could clearly be differentiated from the γ-Al$_2$O$_3$ extrudate. Several previous authors have reported similar results, with the precipitate being possibly attributed to a polymerized $(NH_4)_3Mo_8O_{27}\cdot4H_2O$ surface phase.[7] Similar to aqueous Mo speciation, this precipitation is strongly influenced by the AHM concentration, solution chemistry and pH, and ageing.[7,10] The significant difference in morphology between the extrudate and the precipitate allows easy visual identification of the precipitation problem; subsequent separation of the precipitate from the extrudate was achieved by repeated deionized H$_2$O washing and filtering, and/or sieving. In agreement with previous work, blank IE treatments with γ-Al$_2$O$_3$ extrudates using a lower concentration (0.007 M) AHM solution, resulted in similar Mo loadings with no obvious precipitation.[7]

Use of a bulk, granular powder (such as bulk HTO:Si or Al$_2$O$_3$ powder) precludes any visual identification of precipitation problems.[7] It is therefore possible that the high Mo adsorption capacity of the HTO:Si material might be at least partly attributed to surface precipitation. Further experiments will be performed in the future to confirm whether ion exchange/adsorption or precipitation of Mo species dominates in the case of the HTO:Si material.

Results of the pyrene hydrogenation experiments are shown in Figure 1. The first order hydrogenation activities are calculated on both a catalyst weight basis and on a weight of total active metals basis, i.e. molybdenum and nickel. The activity of both the bulk NiMo/HTO:Si and the Amocat 1C catalysts are based on large historical databases. As shown in a previous paper, the activity of the bulk NiMo/HTO:Si was

higher than the Amocat 1C catalyst on either basis.[11] A significant development effort resulted in the optimization of bulk NiMo/HTO:Si catalyst activity; key steps in optimizing catalyst performance included the addition of silica to the HTO support, controlled drying procedures, optimizing acidification and Mo and Ni precursor loading conditions, and understanding the catalyst activation process.[4,5,12] The combination of these improvements resulted in an increase in pyrene hydrogenation activity of 2-3X. Transmission electron microscopy (TEM) analysis of these catalysts showed that the NiMo/HTO:Si catalyst possesses a higher dispersion of MoS_2 than typical commercial catalysts. A second possible explanation for the higher activity is the higher acidity of the NiMo/HTO:Si as compared to commercial Amocat 1C supported on alumina.[11]
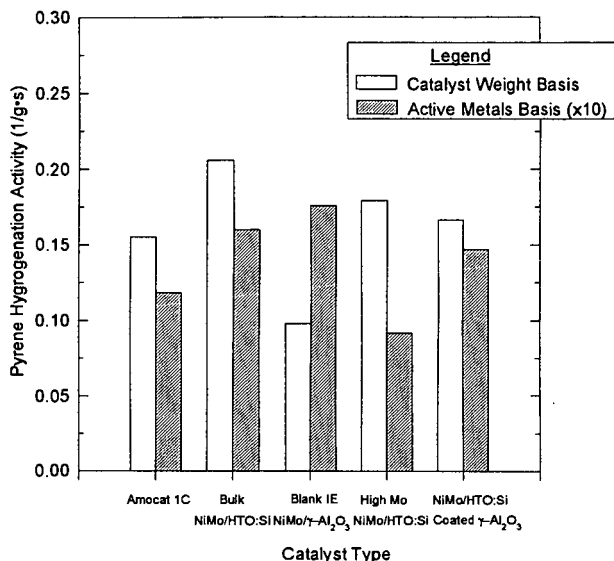

Figure 1. Pyrene Hydrogenation Activity of Commercial and Hydrous Metal Oxide Catalysts

For the other catalyst types, duplicate batches were prepared and tested to ensure representative data; with average values represented in Figure 1. Interesting results were observed for the two extreme cases which simulate NiMo/HTO:Si coated γ-Al_2O_3 IE conditions. For the NiMo/γ-Al_2O_3 catalyst, a low pyrene hydrogenation activity was observed on a catalyst weight basis, but when normalized on a metals basis this proved to be a very active catalyst. This is consistent with the fact that higher MoS_2 dispersions would be expected at lower weight loadings. The high Mo bulk (~15 wt.%) NiMo/HTO:Si catalyst had a slightly lower pyrene hydrogenation activity on a catalyst weight basis than the standard bulk NiMo/HTO:Si catalysts. This is in agreement with previous data suggesting that pyrene hydrogenation activity does not continue to improve with Mo loadings in excess of 10 wt.%.[5] The significant decrease in catalyst activity of this catalyst on a metals basis probably indicates that the MoS_2 dispersion is significantly lower for this sample relative to the standard (8-10 wt.% Mo) bulk NiMo/HTO:Si catalysts. Significant microstructural evaluation is necessary to confirm our speculation regarding changes in MoS_2 dispersion for these samples.

The results for the NiMo/HTO:Si coated γ-Al_2O_3 catalyst proved to be interesting with respect to the two extreme cases described above. Since a significant amount of Mo was used in the Mo IE procedure, it is plausible that both the HTO:Si coating and the

γ-Al$_2$O$_3$ extrudate surfaces were at least partially loaded with Mo by ion exchange/adsorption. Preliminary TEM examination shows the existence of MoS$_2$ on both HTO:Si and γ-Al$_2$O$_3$ surfaces. Given the results shown for the NiMo/γ-Al$_2$O$_3$ and bulk NiMo/HTO:Si catalysts, it is probable that the MoS$_2$ associated with the HTO:Si coating is responsible for most of the activity of the NiMo/HTO:Si coated γ-Al$_2$O$_3$ catalyst. Finally, although the NiMo/HTO:Si coated γ-Al$_2$O$_3$ support was less active than the standard bulk NiMo/HTO:Si catalyst, it was slightly better (~10%) on a catalyst weight basis and 25% more active on a metals basis compared to the commercial Amocat 1C catalyst. These results are significant since this activity was achieved with a lower catalyst cost with respect to bulk NiMo/HTO:Si catalysts. Cost savings would be realized due to a decreased use of metal alkoxides and Mo in the case of the NiMo/HTO:Si coated γ-Al$_2$O$_3$ catalyst.

Future work will be focused in three areas: quantifying HTO:Si coating coverage and optimizing coating techniques, identifying the nature of ion exchanged/adsorbed Mo species on both γ-Al$_2$O$_3$ and HTO:Si surfaces, and careful TEM examination of extrudate surfaces to determine the distribution of HTO:Si coating and MoS$_2$ partitioning between the extrudate and HTO:Si coating surfaces.

CONCLUSIONS
For hydrogenation of pyrene, bulk NiMo/HTO:Si catalysts have been developed that perform better than a commercial benchmark catalyst (Amocat 1C) on either a catalyst weight or active metals basis. This preparation process has been extended to produce NiMo/HTO:Si-coated γ-Al$_2$O$_3$ extrudate with intermediate catalytic activity with respect to Amocat 1C and bulk NiMo/HTO:Si catalysts. Controlled experiments which simulated the Mo ion exchange conditions for the NiMo/HTO:Si-coated γ-Al$_2$O$_3$ catalyst with either bulk HTO:Si or γ-Al$_2$O$_3$ extrudate showed that ion exchange/adsorption of Mo is possible on both. Higher Mo loadings with higher catalyst activity (catalyst weight basis) were obtained on the HTO:Si than the γ-Al$_2$O$_3$ extrudate, indicating that the catalyst activity of the NiMo/HTO:Si-coated γ-Al$_2$O$_3$ catalyst is dominated by the MoS$_2$ present on the HTO:Si coating. Future experiments are in progress to provide additional chemical and microstructural evidence to support these findings.

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The Effect of Promoter Metal Concentration on the Catalytic Activity of Sulfated Hematite for the Liquefaction of a Subbituminous Coal

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Abstract

The application of dispersed iron-based catalysts to the liquefaction of low rank coals has been well documented since the 1930's. More recent research has attempted to improve their activity, primarily by reduction in the particle size or by modification through the introduction of various promoters. The use of sulfated hematite has been shown to yield positive results for the liquefaction of a subbituminous coal. The addition of promoter metals such as molybdenum and tungsten were shown to effect further improvements in activity. This study has shown that the addition of promoters in combination, such as nickel with molybdenum, may significantly increase activity at low promoter concentrations and, potentially, low cost. The effects of the promoter metals nickel, cobalt, tungsten, and molybdenum, individually and in combination will be presented. Molybdenum showed the highest increase in activity for the single promoter metals examined. While the activity of tungsten and cobalt, when used in combination with molybdenum, appeared to be essentially additive, the combination of nickel and molybdenum exhibited a synergistic effect, resulting in high conversions at low promoter loading.

Introduction

Iron-based catalyst precursors have long been known to improve the conversion of low rank coals. Efforts to improve the activity of these catalyst has centered primarily on attaining very small particle size, improved dispersion, and chemical modification of the catalyst. The use of oil-soluble precursors, such as iron carbonyl, have demonstrated significant catalytic activity, presumably through their being efficiently dispersed in the coal-solvent slurry.. However, one study found that an oil-soluble precursor could lead to the formation of large crystallites more rapidly than a small particulate precursor.[1] The loss of dispersion is expected to be associated with a reduction in catalyst activity.

Small particle iron oxides have been shown to have moderate activity for coal liquefaction. The addition of sulfate groups to hematite (Fe_2O_3) has been shown to further improve the activity of these catalysts.[2][3][4][5][6] Sulfated hematites have been produced by two methods. The first involves the addition of a source of sulfate ion to a previously formed goethite (FeOOH) particle by washing with sulfuric acid.[5] The second method involves the precipitation of goethite in the presence of a source of sulfate ions.[7] The particles may then be calcined to form Fe_2O_3/SO_4^{2-}. The nomenclature used does not denote a stoichiometric relationship between the iron and sulfate group but rather indicates SO_3 chemisorbed on the surface of the iron oxide. Both methods of preparation have been shown to yield improved activity for iron oxide catalyst precursors.

The high catalytic activity of molybdenum is well established. However, the use of a dispersed molybdenum catalyst in a coal dissolution process is cost prohibitive, except in very low concentrations, due to difficulties associated with catalyst recovery. Pradhan and coworkers found that the addition of up to 5 wt% molybdenum or tungsten based on iron as a promoter to sulfated hematite resulted in a significant increase in activity.[8] As with most iron-based catalysts the addition of a source of sulfur is critical to achieving the maximum activity. The promoted sulfated hematites demonstrated significant activity at low catalyst loadings (<0.4 wt% iron on coal).

The purpose of the current study was to determine the effect of promoter metals on the

activity of sulfated hematite when used singly and in various combinations. Molybdenum, tungsten, nickel, and cobalt were utilized based on their catalytic activities in other systems.

Catalyst Synthesis

The iron based catalysts used in this study were prepared using an aqueous precipitation technique. This method involves the coprecipitation of iron and a promoter metal in the presence of sulfate ions. Urea was used to effect the precipitation of ferric ammonium sulfate (iron alum), following the method of Kotanigawa et al.[7] Molybdenum was incorporated by addition of ammonium molybdate to the iron alum solution, as described previously.[9] Ammonium nickel sulfate hydrate and cobalt sulfate hydrate were used to add nickel and cobalt, respectively. The precipitated catalysts were filtered and dried in an air flow oven overnight, and then calcined in air at 475 °C for 30 minutes.

The promoted sulfated hematite catalysts were analyzed by XRD, XPS, TEM, SEM, and nitrogen BET adsorption. The results of electron microscopy have shown that the catalysts consist of loose agglomerations of particles with an acicular shape and average dimensions of ~10x50 nm. Surface areas were measured by nitrogen BET adsorption and were found to be in the range 100-200 m^2/g. The addition of up to 10 wt% of molybdenum had little effect on the particle size and no apparent effect on the major phase identified by XRD, to be α-FeOOH with trace α-Fe also present in the as formed precipitate. After calcination, the major phase was α-Fe_2O_3 with some α-Fe still present. The relative amount of α-Fe does not appear to be affected by calcination.

Elemental analysis of the sulfated hematites indicated that the sulfur content was between 2-6 wt%. It has been reported that the sulfur is present on the surface of the hematite as chemisorbed SO_3. Analysis by XPS supported this supposition, showing that the surface sulfur concentration was significantly higher than in the bulk. It was also found that the sulfur content decreased with increasing molybdenum concentration. This may indicate that molybdenum is chemisorbed as MoO_3 displacing the sulfur on the surface. The XPS studies further show that the surface concentrations of molybdenum, sulfur, and tungsten are substantially higher than the bulk concentrations. Nickel and cobalt, on the other hand, have similar bulk and surface concentrations indicating that they may be substituted into the iron oxide matrix. Table 1 shows a comparison of bulk and surface concentrations for a nickel-molybdenum promoted sulfated hematite, clearly demonstrating this result. It follows from Goldschmidt's rules of substitution that the hexavalent ions, Mo, W, and S cannot substitute for iron while the nickel and cobalt can.[10]

Experimental

The catalytic activity of the particles for the liquefaction of Black Thunder subbituminous coal in tetralin was determined using 50 ml horizontal microautoclave reactors. In these experiments, the reactors were loaded with 3 g of as-received coal, 5 g tetralin and 0.07g dimethyldisulfide (DMDS) added as a sulfiding agent. The catalyst was added at an iron loading of 1 wt% with respect to maf coal. The reactors were sealed and pressurized to 1000 psig (cold) with hydrogen, then agitated in a heated fluidized sand bath at 400 cycles/minute. The reactions were carried out at 415°C for 60 minutes, after which the reactors were quenched in a cool sand bath. The use of this system allowed rapid heating and cooling of the reactor thereby reducing errors associated with prolonged heating times.

The total conversion was defined by THF solubility while the THF soluble-pentane insoluble product was defined as preasphaltenes + asphaltenes (PA&A). The THF insoluble product was defined as IOM and the pentane soluble fraction as oils. The total conversion as well as PA&A yield were determined directly and the oil yield was determined by difference. The gas yield was determined directly by gas chromatography. All conversions are reported on a maf coal basis.

Results

The use of the sulfated hematite resulted in an increase in total conversion to 88.1% from 84.8% for the blank thermal baseline conversion. The increase in conversion was due entirely

to an increase in PA&A yield from 42.0% to 46.4% with no substantial change in oil or gas yield. Under the conditions used in this study, the gas yields were unaffected by any of the catalysts. These results were comparable to those obtained using a super fine iron oxide (SFIO) catalyst at similar iron loadings. The SFIO catalyst is of smaller diameter (3 vs 19 nm) and has a higher surface area (190 vs 100 m^2/g) than to the sulfated hematite.

Figure 1 shows the effect of molybdenum concentration on the conversion of the Black Thunder coal in tetralin. The addition of 1 wt % molybdenum as a promoter metal to the sulfated hematite resulted in no significant increase in total conversion. However there was a slight increase in selectivity increasing the oil yield from 34.4% to 38.6%. The molybdenum concentration of 1 wt% with respect to iron corresponds to a loading of 100 ppm molybdenum on an maf coal basis. At this low loading the effect of molybdenum is very modest.

Increasing the promoter concentration to 5 wt% molybdenum on iron resulted in an increase in total conversion to 92% compared to 88% for the unpromoted sulfated hematite. Further, an increase in oil yield and a decrease in PA&A yield was also observed. This represents a significant improvement in the activity and selectivity of the sulfated hematite at a molybdenum loading of only 500 ppm on maf coal.

Increasing the promoter concentration to 10 wt% molybdenum on iron resulted in a further increase in both conversion and selectivity. The increase in total conversion arises from an additional increase in oil yield and a decrease in PA&A yield. The net effect of the addition of 1000 ppm molybdenum on maf coal loading is to increase total conversion by 6% and oil yield by 14% compared to the unpromoted sulfated hematite.

The addition of 1.4 wt % nickel resulted in a slight increase in total conversion over the unpromoted case, unlike the other singly promoted catalysts. This increase was due entirely to an increase in PA&A yield, as the oil yield remained unchanged (within experimental error). In contrast, the other metals produced substantial increases in oil yield. The addition of 2.5 wt % cobalt caused a negligible increase in total conversion but a slight increase in oil yield. The effect of 4 wt % tungsten yielded the same results as the 2.5 wt % cobalt, within experimental error. Therefore, of these three metals, it is found that 500 ppm tungsten and 250 ppm cobalt (maf coal) have very similar catalytic activity for coal liquefaction, while 140 ppm nickel (maf coal) had slightly higher activity for total conversion but lower selectivity to oils.

Of the singly promoted hematites, molybdenum displays the highest activity for conversion and also the greatest selectivity to oils. Further, both the activity and selectivity of the catalyst increase with increasing molybdenum concentration. However, due to the significant cost associated with molybdenum, a loading of 1000 ppm on maf coal would be prohibitively expensive. Therefore the use of other promoters in combination with molybdenum was explored.

Cobalt /molybdenum doubly promoted sulfated hematite demonstrated considerable catalytic activity. As shown in Figure 2 the addition of 1 wt % molybdenum and 0.5 wt % cobalt (based on iron) to the sulfated hematite increased the total conversion to a level close to that obtained with 5 wt% molybdenum, and greater than that obtained with 2.5 wt % cobalt alone. This may indicate a possible synergistic effect between the molybdenum and the cobalt promoters. The oil yield was increased to 40 %, only slightly higher than the oil yield obtained with 1 wt % Mo. Thus, at a promoter concentration of 100 ppm molybdenum and 50 ppm cobalt (maf coal), the activity of the catalyst for total conversion approaches that of 500 ppm molybdenum, with slightly lower selectivity to oils.

Similar results were obtained for hematite doubly promoted by molybdenum and tungsten. The addition of 1 wt% molybdenum and 0.8 wt % tungsten gave a total conversion of 92 % and an oil yield of 40%. In Figure 3, the molybdenum/tungsten promoted catalyst is compared to singly promoted molybdenum (5wt%) and tungsten (4wt%) catalyst. In combination with molybdenum, cobalt and tungsten appear to have similar effects.

A combination of nickel and molybdenum yielded somewhat better results. The use of 0.9 wt

% molybdenum and 0.7 wt% nickel as promoters produced marginally higher total conversion than the cobalt/molybdenum and tungsten/molybdenum promoters. More importantly, however, is the fact that very high oil yields were obtained. As shown in Figure 4, the oil yield exceeds that obtained with 5 wt% molybdenum and strongly suggests a synergistic effect between the nickel and molybdenum. The combination of 90 ppm molybdenum, 70 ppm nickel, with 1 wt% iron on maf coal gave the highest selectivity to oils of the doubly promoted catalysts tested.

The promising results of these studies have prompted further interest in these catalysts. By varying the concentration of promoter metals it may be possible to obtain higher conversions or, more probably, to increase the selectivity to oils. Studies are currently underway to optimize the promoter metal concentrations to maximize catalytic activity and selectivity.

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Table 1. Elemental Composition of Promoted Sulfated Hematite.

Element	Bulk wt %	Surface wt %
Molybdenum	4.0	7.5
Nickel	2.3	2.5
Sulfur	2.7	4.7

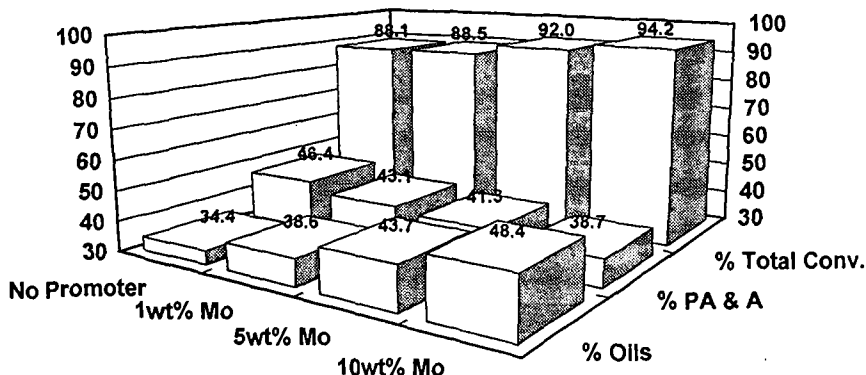Figure 1. Effect of Molybdenum Loading on Conversion

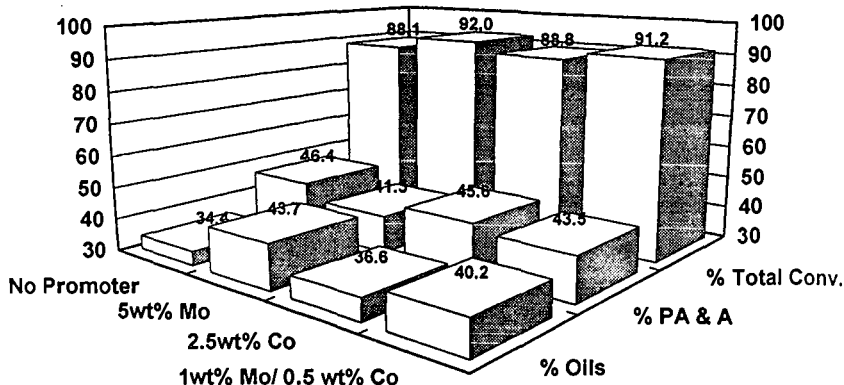Figure 2. Effect of Molybdenum and Cobalt on the Activity of Sulfated Hematite

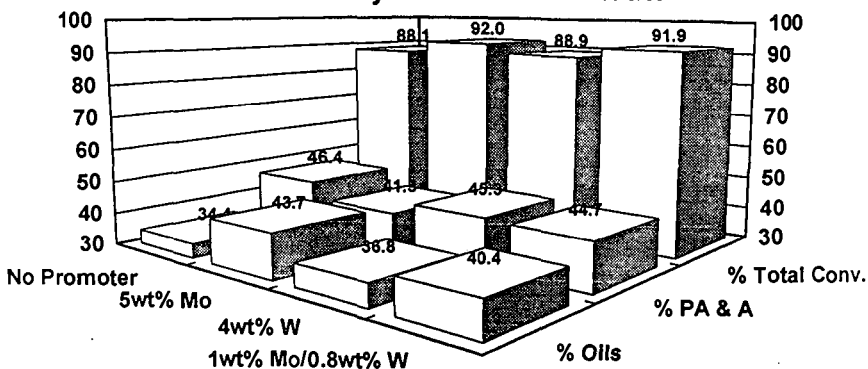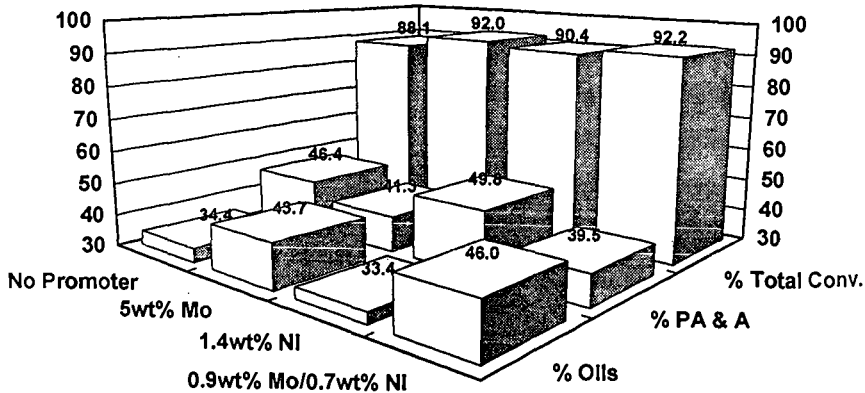Figure 3. Effect of Molybdenum and Tungsten on the Activity of Sulfated Hematite

Figure 4. Effect of Molybdenum and Nickel on the Activity of Sulfated Hematite

TOWARDS IMPROVED IRON-BASED CATALYSTS
FOR DIRECT COAL LIQUEFACTION

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INTRODUCTION

Iron-based catalysts for direct coal liquefaction (DCL) have
several advantages: they are cheap and environmentally benign,
and have a reasonable activity in the sulfide form. Work in this
area has recently been collected and published [1].

Work in our laboratory has focussed on catalysts made with ferric
sulfide as a precursor. This material is unstable even at room
temperature, and disproportionates to form pyrite (FeS_2; PY),
non-stoichiometric pyrrhotite (FeS_x, $x \sim 1$; PH), and elemental S
[2]. The value of x and the relative amounts of PY and PH depend
upon the time and temperature of disproportionation [3,4].
Materials from hydrothermal disproportionation at 200°C for 1 h
have roughly equal amounts of PH and PY (on an iron basis), and
these materials appear to make the most active and selective
catalysts for DCL [3,5]. These catalyst precursors and catalyst
materials have been characterized by atomic adsorption
spectroscopy (AA), Auger electron spectroscopy (AES) and x-ray
diffraction (XRD). The characterizations have been correlated to
the reactions of Fe during disproportionation and to the
performance of the catalysts [4,6].

Improvements in these catalysts can be made in two ways: by
altering the active sites, and by decreasing the particle sizes.
In the present work, we present examples of both types. The
active sites are altered by using small amounts of a second
metal. The particle sizes are reduced by using an aerosol
technique for preparation.

AEROSOL-BASED PREPARATION OF IRON CATALYSTS

Advantages of the aerosol process have been described earlier
[7]. Besides generating particles of small size, the process is
inherently scalable (so that large quantities of catalyst are
possible). Further, the solvent need not be aqueous, and the
potential exists for making materials not stable under other
conditions.

A sketch of the apparatus is shown in Figure 1. A solution of a
ferric salt, typically acetate, is pumped at high pressure
through a nozzle to a reactor. The micron-sized droplets react
with H_2S in the vapor phase (as 10% of an H_2S/N_2 mixture) to form
ferric sulfide at the interface. At the high temperatures
involved, water evaporates from the liquid droplet. Hence the
particle may be an annulus or a solid sphere. The ferric sulfide
quickly reacts to PY, PH and elemental sulfur. The final size
achieved depends upon the pump pressure, the diameter of the
nozzle orifice, the viscosity and surface tension of the liquid,
the concentration of reactants in liquid and vapor phases, and
the effect of pH and anion basicity on the reaction rate. The
particles stay in the reactor, where they are collected in
tetralin; the vapor bubbles through an NaOH scrubber before being
safely vented. The particles, collected after the process is
complete, have been characterized and used for DCL.

XRD data, taken in the laboratory of Professor M.S. Seehra at
West Virginia University, indicate interesting effects when
conditions are changed. At low precursor conditions, 0.01M, when
aerosol reactor conditions are maintained at 200°C and 200 psi,
peaks are observed corresponding to FeS_2, monoclinic pyrrhotite
(Fe_7S_8, i.e., $x = 1.143$) and elemental S. This is consistent with
XRD patterns obtained using earlier preparation techniques such
as hydrothermal disproportionation [3,4]. However, when the

precursor concentration is higher, 0.1M, and the temperature is 165°C, peaks observed include not only FeS_2 and S but now greigite (Fe_3S_4, $x = 1.333$). But greigite is stable typically only below 100°C [8]. Perhaps the thermodynamically unstable form is trapped in the particle due to the rapid quenching that takes place in the aerosol reactor. The role of the higher precursor concentration in facilitating the unstable form is not clear.

Other characterization data can be found in Table I. The samples are characterized in terms of the precursor concentration as well as the pressure and temperature in the reactor. Density was measured using He pycnometry. For sample 9, grinding the solid increased the density measurement by 0.1 g/cc, probably within the accuracy of the measurement. Hence the values measured are those of the density of the actual material, whether present as a solid or an annular shell, and not the bulk density of an annular shell. Accordingly, the changes in density between samples 8 and 9 and between samples 9 and 10 are related to the different solids produced under those two conditions, not changes in the inner and/or outer diameters of the particles. Note that increasing the temperature of the aerosol reactor causes less change than increasing the precursor concentration.

The mean diameter in Table I is measured using multiple-angle laser light scattering with photon correlation spectroscopy. For these measurements, the particles were suspended in tetralin, the same solvent used for the DCL experiments. In addition, a transmission electron microscope (TEM) in Professor G.P. Huffman's laboratory at the University of Kentucky was used. In the latter measurements, the particles were suspended in ethyl alcohol, which was then evaporated on the TEM slide. Sizes measured by TEM range from 3 - 580 nm, with a majority of particles in the lower portion of the range. The 1-2 orders of magnitude by which the two techniques differ is probably due to clumping of the particles in the tetralin. Since the physical situation with tetralin is closer to the conditions during liquefaction, the values in Table I are probably more realistic than TEM values. The larger particle size observed in sample 9 relative to sample 8 is probably due to the increased concentration of precursor used.

Bulk ratios of S to Fe and the corresponding surface ratios, obtained from energy-dispersive x-ray spectroscopy (EDX) and AES respectively, are also shown in Table I. Bulk ratios for samples 7 and 8 are similar, and greater than 1.5, the value expected for Fe_2S_3. A smaller value is obtained for sample 12, and the value decreases further for sample 9. The decreasing values may be due to loss of elemental S (found after disproportionation of the Fe_2S_3) in sample handling. Hence the decreasing values may indicate increasing amounts of elemental S formed, and increasing amounts of PH relative to PY. The decreasing bulk values are consistent with decreasing surface S/Fe values as well. The ratios are higher on the surface than in the bulk, again consistent with the formation of elemental S and its migration to the surface. The AES peak shape corresponding to S is, in fact, characteristic of that ascribed to elemental sulfur.

The performance of these catalysts in DCL is shown in Table II. The experiments were carried out at 350°C and 1000 psi H_2 (cold) for 1 h using DECS-6 coal in tetralin with 0.1 ml CS_2 added. The catalyst loading was 5% and the reactor was agitated vertically at 500 rpm. Full experimental details have been provided earlier [3,4]. All catalyst samples used show noticeable improvements in conversion and asphaltene yield relative to the thermal runs, although oil yields are not improved. The improvement in conversion is most striking for catalysts prepared using the lower precursor concentration, and the oil yield is best for the catalyst prepared at the highest temperature.

MULTI-METAL IRON-BASED CATALYSTS

The Hume-Rothery rules (of thumb) govern which metals can be substituted into an existing lattice. The major requirement is that the substituent and the original metal should have ionic radii no more than 15% apart. For the Fe ion, this requirement provides a large number of potential substituents. For any of these to be useful, conversion and/or oil yield should increase at least marginally when the material is used as a DCL catalyst,

and the material should be only marginally less attractive, economically and environmentally, than the iron-alone catalyst. Because of space constraints, we report here only on Fe-Ni-S catalysts. However, preliminary data have been gathered when other metals have been used, including Co, Mg, Mo and Cu.

Because of the long set-up times required for the aerosol reactor, the Fe-Ni-S catalysts were not prepared in this manner. Instead, variants of the old hydrothermal disproportionation technique [3,4] were used. When relatively low disproportionation temperatures, T_d, were required, appropriate ratios of $FeCl_3$ and $NiCl_3$ solutions were combined with Na_2S in a glass ampule in a cold room. This formed the precursors instantaneously as a gelatinous precipitate. For disproportionation of the ferric sulfide, the ampule was then sealed and placed in an autoclave containing water. The autoclave was maintained at T_d, equal to 200°C or 250°C, for 1h. The presence of high-temperature steam at equal pressure on both sides of the ampule prevented it from being destroyed. The ampule seal was broken and the material washed (to remove NaCl formed as a byproduct) and vacuum-dried. When a high-temperature disproportionation (HTD) was required, the precursors formed as above were washed and dried first, then heated (at 350°C or 375°C) for 15 min. in 1500 psig H_2 (hot). In both cases, the material was formulated to have nickel fractions (Ni/{Ni + Fe}) of 0.0, 0.01, 0.1, 0.5, 0.9 and 1.0.

DCL results for a series of the Fe-Ni-S catalysts are shown in Figure 2. Reaction conditions are the same as those in Table II. Conversions using these catalysts go through a shallow maximum between nickel fractions of 0.1 and 0.5, regardless of the T_d value. For T_d = 200°C, the oil + gas yield passes through a minimum with increasing nickel fraction. Hence this is clearly not a viable catalyst, even though the corresponding catalyst in the absence of Ni was shown [3-5] to be the preferred catalyst. For T_d = 375°C, the yield passes through a maximum corresponding to a nickel fraction of 0.5. Since the yield and the conversion of this HTD catalyst are superior to any other in Figure 2, this is the preferred catalyst in the Fe-Ni-S family.

Figure 3 represents XRD peaks for this HTD catalyst and for the two extreme values of the nickel fraction. The XRD pattern for the catalyst containing Fe alone shows stronger pyrrhotite peaks than those corresponding to the catalyst hydrothermally disproportionated at 200°C. This is consistent with the higher value of T_d and the presence of H_2 during disproportionation. When Ni alone is present, the XRD peaks correspond to those of Ni_3S_2. However, when both Ni and Fe are present, a completely different pattern is seen. The major peaks correspond to those of $(Fe,Ni)_9S_8$. Hence, XRD indicates that the present method of forming multi-metal catalysts results in alloy formation, not just a combination of two sulfides. The alloy appears to result in higher conversion and yield when used as a catalyst in DCL.

AES data for the HTD catalyst are shown in Figure 4 as a function of nickel fraction. The nickel fraction on the surface is never higher than the fraction in the bulk. This implies that, at all levels of nickel formulation, the nickel is preferentially found in the bulk, not the surface. S is enriched on the surface relative to the bulk, since almost all values can be seen to be greater than 1.5. However, comparing the values with that for zero nickel fraction indicates that there is less S on the surface when Ni is present than when it is absent. Further, comparing the latter value with those from Table II indicates that an aerosol catalyst typically contains more S on the surface than does the HTD catalyst. Finally, it is worth noting the complementary nature of the curves for S and for O. If the S and O fractions are added, the numbers correspond to the surface S/Fe ratios for the aerosol catalyst. Since oxygen is not present in the formulation, oxidation must be occuring during handling. The role, if any, of the surface oxygen on the catalytic properties of the materials deserves further investigation.

SUMMARY AND CONCLUSIONS

Iron-based sulfide catalysts can be modified to improve their performance in DCL. Preparation using an aerosol formulation results in small particle sizes and the possiblity of forming thermodynamically unstable structures. Preparation using Ni as a

second metal results in multi-metal sulfides being formed. With both techniques, surface characterization correlates well with DCL results. Surface oxidation may be affecting the catalytic behavior of these materials.

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ACKNOWLEDGMENTS

TABLE I
Characterization of Aerosol-Generated Catalysts

SAMPLE #	PRECURSOR CONC, [M]	PREP PRES [psi]	PREP TEMP [°C]	DENSITY [g/cc]	DIA [nm]	BULK S/Fe EDX	SFCE S/Fe AES
7	0.01	200	200	---	---	2.5	3.6
8	0.01	100	200	4.60	507	2.5	3.3
9	0.10	100	200	4.27	1200	0.9	2.0
12	0.01	100	250	4.66	---	1.9	---

TABLE II
DCL with Aerosol-Generated Catalysts

SAMPLE #	CONVERSION [%]	ASPHALTENE YIELD [%]	OIL + GAS YIELD [%]
thermal	54.9	41.2	13.6
8	64.9	55.6	9.3
9	63.0	52.1	10.8
12	64.4	54.8	10.9

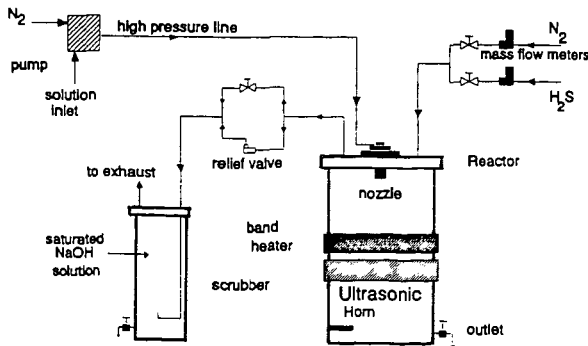FIGURE 1. Apparatus for generation of aerosol particles of catalyst.

FIGURE 2. DCL using Fe-Ni-S catalysts, as a function of T_d, disproportionation temperature, and nickel fraction, Ni/{Ni+Fe}.
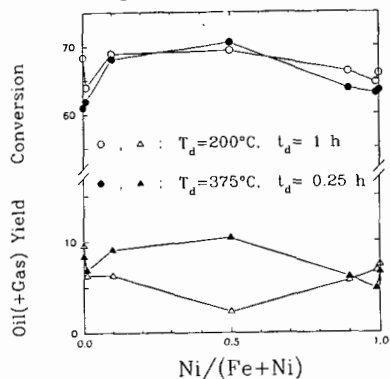

FIGURE 3. XRD for HTD catalyst with Ni/{Ni+Fe} = 0 (bottom), 0.5 (middle), and 1.0 (top).
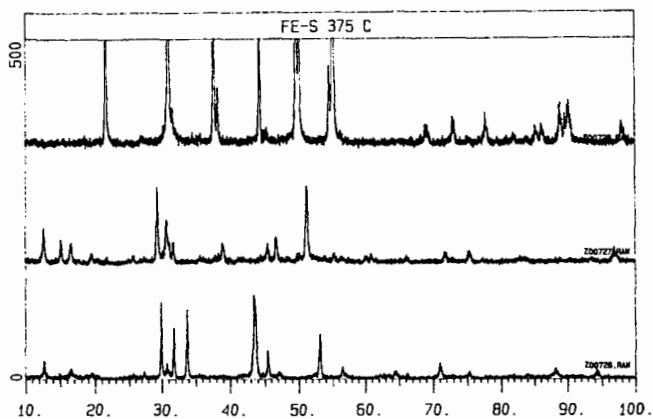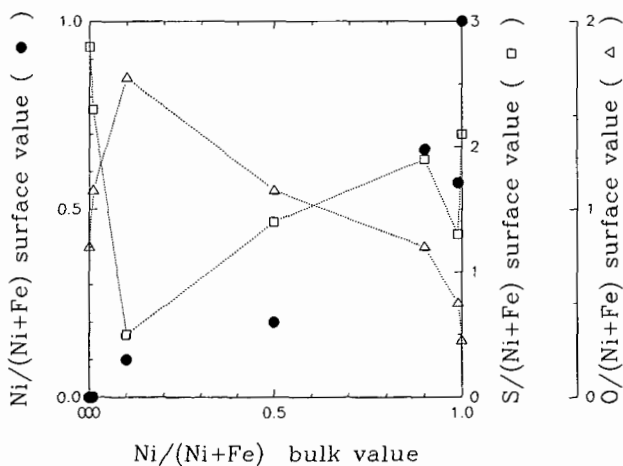

FIGURE 4. AES for HTD catalyst as a function of Ni fraction.

IMPREGNATION ALTERNATIVES FOR Fe-BASED COAL LIQUEFACTION CATALYSTS

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Introduction

Because of the cost effective and environmentally compatible nature of Fe, attention has been directed towards improving the utilization of this metal in direct coal liquefaction. Among the several factors thought to affect catalyst activity, much of this work has focused on dispersion. Weller and Pelipetz[1] reported the importance of catalyst dispersion, based on experiments with a wide variety of catalysts in solvent-free liquefaction studies. And in the presence of solvent, other studies have demonstrated the advantages of adding the precursor by impregnation over its addition in the form of particulates. In general, a high surface/volume ratio, along with intimate contact between the active catalyst and coal, are thought to be the controlling factors.[2] Dispersion, as normally inferred from changes in catalyst activity, may be affected by the mode of addition, the presence of solvent, and the initial composition of the precursor (e.g., soluble organometallics); and for coal-impregnated catalyst precursors, the choice of impregnation solvent[3] and impregnation conditions.

A variety of innovative strategies have been developed to introduce catalyst precursors to the liquefaction reaction while seeking to maintain particle size and distribution. These have included the use of emulsions and colloids,[4,5,6] direct addition of ultra-fine particles to the slurry,[7,8,9,10] addition of oil soluble organometallics and carbonyls,[11,12,13] ion exchange[14] and impregnating the coal.[1,15,16]

One of the more effective ways of introducing an Fe catalyst precursor to the coal liquefaction process is to disperse the iron salt onto the coal surface using a liquid medium to impregnate the feedstock. In one technique, coal is impregnated with a metal salt solution up to the point where the unbound moisture begins to form drops.[17] Additionally, the Fe salt may be precipitated with a base solution to fix the precursor onto the coal surface, called incipient wetness/ precipitation (IW/P). Cugini and his co-workers,[15] using ferric nitrate and ammonium hydroxide, recorded the benefits of this last method of preparation, which included high Fe dispersion levels and exploiting the sub-micron particle size of the FeOOH precursor, and follow-on active pyrrhotite phase. Andres, et al.,[18] earlier verified that iron particles, in various forms as oxides and oxyhydroxides, retained their small size upon conversion to pyrrhotite under coal hydroliquefaction conditions.

The IW/P preparation is a multistep process, consisting of coal preparation, metal impregnation, base precipitation, filtration, washing, and drying. The influence of these various steps on coal surface chemistry and liquefaction performance was reported previously.[19] XPS studies showed the iron on IW/P coals to be highly dispersed, more concentrated on the coal surface, and present as both FeOOH and Fe_2O_3.

Because of the cost of the several processing steps and related material handling requirements, the promise of IW/P coal preparation may not be realized commercially without some simplification. In the case of Mo, studies have suggested that complete dispersion of the catalyst precursor at the outset of the reaction may not be essential for satisfactory results. Bockrath, et al.,[20] recognized that molybdenum sulfide concentrated in THF extracted liquefaction residues retained its catalytic activity when mixed with fresh coal slurry. In related work, molybdenum was impregnated onto coal which was then exposed to liquefaction conditions in a microautoclave. The products, which were subsequently mixed with 20 times as much fresh coal, were found to be active even in the initial stages of liquefaction.

The work presented here addresses impregnation alternatives which reduce the amount of prepared coal by loading the precursor Fe on only a fraction of the feedstock. Concentrating the Fe on only a portion of the feed, referred to here as the "vector", would reduce the cost of handling the coal, which could be a significant factor in the overall economics of the project. Additionally, if the metal added in this way remains quite active, other more robust and/or active substrates might be considered as the catalyst carrier. Since it had been determined that ferrous sulfate is currently the lowest cost form of soluble iron commercially available (as copperas), work was performed

exclusively with this salt.

Experimental

Materials- Reagents were purchased as follows: Practical grade dimethyl disulfide (DMDS) from Fluka AG; 99% purity UV grade tetralin, high purity tetrahydrofuran (THF), and high purity pentane were Burdick & Jackson Brand from Baxter S/P; 98% purity $FeSO_4 \cdot 7H_2O$ from Aldrich; and concentrated ammonium hydroxide from Mallinkrodt. Ultra High Purity Grade hydrogen was supplied by Air Products and Chemicals, Inc. Burn Away$_{TM}$ petroleum coke was supplied by HRI, Inc. Coulometrics brand carbon black, commercially reduced in a 95% N_2/ 5% H_2 gas stream at 400°C, was purchased from UIC Inc. The coke and carbon black are described further in Table I, which shows they are predominantly fixed carbon. Wyodak subbituminous coal from the Black Thunder mine, supplied by CONSOL, Inc., was ground to -200 mesh, riffled and stored under nitrogen at 4°C. The analysis of the coal (dry basis) was: C- 72.2 %; H- 4.3%; N-1.2%; S- 0.5%; O (by difference)- 16.0%; ash- 5.8%. It had a moisture content of about 21 wt%.

Preparation of vectors- Four coal samples were impregnated with Fe using the IW/P technique. The first (termed 100% IW/P) had an Fe concentration of 0.8 wt% mf coal. The other three were impregnated with additional Fe sufficient to mix them with fresh coal in the proportions of 10:90, 50:50, and 90:10, to yield an overall Fe concentration the same as the 100% IW/P sample. The coke and carbon black were also prepared using the same IW/P technique as for the coal, at concentrations that would allow the Fe to be added on 10 wt% of the reactor feed. The 100% IW/P sample and the mixed feed coals were then liquefied to compare product yields among the various ways Fe had been introduced to the reaction.

For each vector prepared, the $FeSO_4 \cdot 7H_2O$ required was dissolved in 0.76 g H_2O/g vector coal (dry basis). The solubility of ferrous sulfate presented no problems in the preparations. This solution was added dropwise while stirring and then allowed to stand for ¼ hour. A 3% ammonium hydroxide solution was added at a ratio of 138 mol NH_3/mol Fe and filtered. The filter cake was washed with 25 ml distilled water/g coal until the odor of ammonia was absent, and dried for 20 hours to about 20% water content with flowing N_2 at 25 °C. Recovery of Fe on the samples was greater than 98%.

Liquefaction experiments- Typical liquefaction experiments were carried out using a total of 3.0 g coal and 5.4 g tetralin in 50 ml microautoclaves. A blend of Fe-impregnated substrate and as-received coal comprised the reactor feed. When Fe was added to the reaction mixture, sulfur, as DMDS, was added at a minimum ratio of 1.5 mol S/mol Fe, sufficient to produce pyrrhotite as the final form of the catalyst. The reactors were pressurized to 6.89 MPa with hydrogen and shaken at 400 cpm in an air-fluidized sand bath at 415 °C for 30 minutes. Experiments were duplicated, at a minimum.

In the first step of product work-up, gases were collected and analyzed by gas chromatography. The other products were then scraped from the reactor with THF and extracted in a Soxhlet apparatus. The THF solubles were subsequently separated into pentane soluble (Oils) and pentane insoluble (PA+A) fractions. Total conversion was determined from the amount of THF insoluble material that remained. Added Fe was subtracted from this residue at the equivalent weight of pyrrhotite. Oils were calculated by difference, and as a result, water produced during liquefaction, as well as any experimental error, is included in that fraction. All product yields are stated on an maf coal basis.

In liquefaction experiments using the coke and carbon black substrates, the substrates (and later, vector) weights were subtracted from the final THF insoluble residues at their mf starting weight, even though both substrates showed a slight propensity (~2-3 wt%) to adsorb THF during Soxhlet extraction. As before, liquefaction product yields were calculated on an maf coal basis.

Results and Discussion

Limited Fe dispersion- To examine very limited dispersion of the starting Fe, the powdered $FeSO_4 \cdot 7H_2O$ was added directly to the reactor without mixing with the coal feed. Additionally, to examine an alternate, simplified preparation similar to the IW/P method, an aqueous solution of the same salt was added directly to the reactor using only 12% the solution weight needed to impregnate the coal by the IW/P method, without base precipitation or drying. The results of these two experiments are shown in Table II in comparison with the thermal conversion of coal (uncatalyzed), and with liquefaction of the 100% IW/P coal. Both the powdered and aqueous Fe additions showed only slight catalyst activity, with any added conversion reporting to the PA+A fraction. In contrast,

impregnating the coal improved THF conversion by 8%. Again the increase in conversion reported primarily to the PA+A fraction; the slight increase in Oils yield is not significant.

Liquefaction with vector coals- To investigate the effects of limited dispersion using IW/P coals, liquefaction experiments were performed by impregnating Fe on the vector portion of the total feed coal. The greater the Fe concentration on the vector portion of the feed mixture, the less disperse Fe is at the outset of the liquefaction experiment. As the Fe and salt concentrations in the vector mixtures show in Table III, the extreme case is the 10% vector, where the Fe concentration was nearly 8% mf coal, equal to 10 wt% salt (as FeOOH). At the start of liquefaction, the iron salt is highly concentrated on this portion of the feed coal, while the other 90% of the coal is relatively iron-free.

Liquefaction results using the vectors mixed with as-received coal are also shown in Table III. THF conversions of the mixed feed coals are all very similar, taken as a group, to the 100% IW/P coal, and clearly higher than the uncatalyzed reaction. Oils yields also appear to be about the same, with a slight advantage for the 10% case, which carried a somewhat higher iron load. Overall, the results suggest that IW/P impregnation of the iron on a portion of the coal does not hinder its availability to participate in the liquefaction reaction in tetralin.

Liquefaction with coke and carbon black substrates- Two stable, non-reactive substrates, coke and carbon black, were selected for comparison with coal, which rapidly dissolves during liquefaction. First, to determine a liquefaction yield background, experiments were performed using the coke and carbon black at 10 wt% of the reaction feed mix, without any added Fe. The coke alone improved coal conversion about 2%, but the carbon black did not affect conversion (see Table IV). As a commercial filtration aid, the coke may have improved Soxhlet extraction of the liquefaction products, or perhaps introduced a trace amount of catalyst material that will be revealed through ongoing analytical work.

After Fe impregnation of the two carbon substrates, SEM studies showed that the larger petroleum coke (see Table I) retained its size and structure after impregnation, but the nanometer-fine structure of the carbon black was lost and resulted in nominal 300 micron agglomerates. These larger agglomerates appeared to be completely coated with the Fe salt, an effect not visible on the coke.

Coal liquefaction experiments were performed as before, with the Fe-laden vectors at 10 wt% of the reactor feed. Iron added on the coke increased THF conversion about 4% compared with its background, as did Fe added to the carbon black. The increases in product yield were 3-4% less than with Fe dispersed on the 10% coal vector, but the yields evidence that Fe distributed on the two stable non-coal vectors participates in the liquefaction reaction.

Conclusions
Very little activity was seen for ferrous sulfate added directly to the reactor either as a powder, or molecularly dispersed in an immiscible aqueous solution. High activity is observed when a coal vector is employed, and we can postulate the effect arises from dispersion throughout the reactor as the coal structure rapidly dissolves. Moreover, if catalyst dispersion may be inferred from its activity, then Fe added on a coal vector comprising only 10% of the feed coal is sufficiently dispersed through the course of a 30 minute reaction to give yields comparable to experiments where Fe is added to the entire feedstock. Some activity is observed when the Fe is dispersed on a carbon substrate that is stable under liquefaction conditions, but not as much as when dispersed on some fraction of the coal itself. However, this activity may be commensurate with the level of dispersion provided by the >100 μm coke and carbon black particles that were added to the reaction system.

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Table I. Non-coal Carbon Substrates Used for Fe Impregnation.

	petroleum coke	carbon black
BET surface area, m²/g	< 1 (non-porous)	90
Particle size, μm (by TEM)	100	.01-.06, in clusters
THF insolubles, wt% mf sample	102.5	102.9
Proximate analysis, wt % as-determined		
Water	1.0	0.8
Ash	trace	3.3
Volatile matter	5.3	2.8
Fixed carbon	93.7	93.1
Total	100.0	100.0

Table II. Effect of Alternate Ferrous Sulfate Addition Methods on Coal Liquefaction.[a]

Additon Method	none	Powdered	Aqueous	IW/P
Added Fe, wt% mf Coal	0	0.79	0.78	0.78
Products, wt% maf Coal				
HC Gases	0.7	0.8	0.9	1.1
$CO+CO_2$	4.7	5.3	4.8	5.7
Oils	33.2	32.2	31.5	34.3
PA+A	37.8	40.0	40.0	43.6
IOM	23.6	21.7	22.8	15.3
THF Conversion	76.4	78.3	77.2	84.7

a. Results of liquefaction studies at 415°C for 30 minutes, 2.3 tetralin:coal ratio.

Table III. Effect of Limited IW/P Fe Dispersion on Coal Liquefaction.

Impregnated Coal/total Coal, wt%	10	50	90	100
Added Fe, wt% mf total Coal	0.81	0.78	0.78	0.78
Vector properties				
Added Fe, wt% mf vector (salt-free basis)	7.59	1.55	0.87	0.78
Added FeOOH, wt% wet vector mixture	10.3	2.0	1.1	0.8
Products, wt% maf total Coal[a]				
HC Gases	1.0	1.0	0.8	1.1
$CO+CO_2$	4.8	4.9	4.7	5.7
Oils	38.2	33.3	32.5	34.3
PA+A	41.1	44.0	44.6	43.6
IOM	14.9	16.8	17.4	15.3
THF Conversion	85.1	83.2	82.6	84.7

a. Results of liquefaction studies at 415°C for 30 minutes, 2.3 tetralin:coal ratio.

Table IV. Effect of Limited Fe Dispersion on Non-coal Vectors.

Substrate	coke blank	coke with Fe	Δ	carbon black blank	carbon black with Fe	Δ
Vector /total mixture, wt%	10	10		10	10	
Added Fe, wt% mf Coal	0.0	0.74		0.0	0.79	
Vector properties						
Added Fe, wt% mf vector (salt-free basis)	0.0	6.10		0.0	6.23	
Added FeOOH, wt% wet vector mixture	0.0	8.6		0.0	9.1	
Products, wt% maf Coal[a]						
HC Gases	0.7	0.5	-0.2	0.6	0.9	0.3
$CO+CO_2$	5.1	4.7	-0.4	5.1	4.7	-0.4
Oils	37.3	38.2	0.9	32.6	38.3	5.7
PA+A	35.7	39.0	3.3	38.2	37.1	-1.1
IOM	21.2	17.6	-3.6	23.5	19.0	-4.5
THF Conversion	78.8	82.4	3.6	76.5	81.0	4.5

a. Results of liquefaction studies at 415°C for 30 minutes, 2.6 tetralin:coal ratio.

LIQUEFACTION OF COAL IMPREGNATED WITH CATALYST DURING PRESWELLING

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ABSTRACT

The effect of impregnating coal with slurry phase catalysts during solvent preswelling on coal conversion was investigated. Black Thunder subbituminous coal which was either untreated or pretreated with aqueous SO_2 was used. The coal was placed into the swelling solvents, THF, methanol or isopropanol, for 96 hr prior to liquefaction. Slurry phase catalysts, Mo naphthenate, Molyvan L and Ni octoate, were introduced into the swelling solvents; catalyst uptake by coal was 90 to 95% of the catalyst introduced. Coal conversions of these impregnated coals were obtained at 410 °C in reaction solvents of 1-methylnaphthalene, coal-derived V1074, and dihydroanthracene, and were compared to those obtained with swelled and nonswelled coals. The swelling solvent and the SO_2 pretreatment affected the amount of coal conversion obtained. Coal conversions achieved with impregnated coals were somewhat less than those achieved when the catalyst was added directly to the reactor.

INTRODUCTION

Increases in the liquefaction conversion and production of upgraded product from subbituminous coal are desirable to make the process a feasible option for production of transportation of fuels. To this end, a process was conceptualized and tested. The conceptual process involves several steps: (1) coal is pretreated with aqueous SO_2; (2) the pretreated coal is then swelled in a hydrogen bonding solvent in which is placed a slurry phase catalyst; (3) during swelling the slurry phase catalyst is deposited within the pores of the coal; and (4) the impregnated coal is liquefied having the catalyst in intimate contact with the reacting coal molecules.

The research described herein tested the conceptual process using both untreated and SO_2 treated coal. The reason that a substantial number of experiments was performed with the untreated coal was that previous results[1] indicated that swelling coal prior to liquefaction was more beneficial to coal conversions of untreated coal than of SO_2 treated coal. Reactions were performed (1) without swelling prior to liquefaction; (2) with swelling prior to liquefaction with the catalyst being added directly to the reactor; and (3) with swelling prior to liquefaction with catalyst being added to the swelling solvent. Three different swelling solvents, tetrahydrofuran (THF), isopropanol, and methanol, were used[2]; three different catalysts, Mo naphthenate, Molyvan L and Ni octoate, were used; and three different reaction solvents, 1-methylnaphthalene, a relatively inert solvent; V1074, a coal-derived solvent and dihydroanthracene, a hydrogen donor solvent, were also used.

EXPERIMENTAL

Materials. Liquefaction reactions were performed using untreated and aqueous SO_2 treated Black Thunder coals. The swelling solvents, THF, methanol, and isopropanol were obtained from Fisher and were used as received. The liquefaction reaction solvents used were 1-methylnaphthalene (1-MN) (98% purity) and 9,10-dihydroanthracene (DHA), which were obtained from Aldrich, and V1074, a coal-derived solvent, supplied by Amoco. The catalysts used were Molyvan L from Vanderbilt Chemical and Mo naphthenate and Ni octoate from Shepherd Chemical Company; and Ni naphthenate from Strem Chemical Company.

Swelling and Reaction Procedures. Untreated and SO_2 treated Black Thunder coals were swelled by introducing 1.33 g maf coal to the swelling tube and then adding 7 ml of solvent. Molyvan L, Mo naphthenate, and Ni octoate catalysts were charged to the swelling solvent at 1.05 times 600 to 800 ppm of active metal, the amount used when the catalyst was added directly to the liquefaction reactions. The coal was then allowed to sit unagitated in the swelling solvent for 96 hr. These experiments were designated with a "N" on the tables. Several experiments, designated with an "A" on the tables, were performed in which the coal and swelling solvent were agitated using an orbital shaken at 250 rpm during the 96 hr swelling period. Molyvan L was also added to the swelling solvent at twice the loading typically used, 1400 to 1600 ppm of active metal. These experiments in which the catalyst level was doubled are designated with a "D" on the tables.

Liquefaction reactions using untreated Black Thunder coal in 1-MN were performed at 410°C for both 20 and 30 min in stainless steel tubular microreactors. The liquefaction reactions for SO$_2$ treated Black Thunder coal in 1-MN and for untreated Black Thunder coal in V1074 and DHA were conducted for 30 min. Each reaction contained ~1.33 g of maf coal, 2 g of solvent, 0.67 g of pyrene (PYR) and residual swelling solvent that remained in the swelled coal. The amount of solvent absorbed in the coal after swelling differed for each swelling solvent. The amount of solvent retained in the coal ranged from 0.6 to 1.0 times the coal mass. The amount of catalyst taken up by coal was obtained for selected reactions using x-ray fluorescence spectroscopy. Hydrogen gas was introduced at 1250 psig at ambient temperature. The reactor was well-agitated at 450 cpm.

Analysis. Products from the liquefaction reactions were removed from the reactor with THF. The conversion of the coal to THF solubles was determined. For the reactions where analysis of catalyst uptake was obtained, the values for the catalyst loading are given, otherwise, the presumed amount deposited ranged from 90 to 95% of the 600 to 800 ppm of active metal loaded on a per gram of coal basis. The amount of PYR hydrogenation to hydrogenated products was obtained by gas chromatographic analyses using a Varian Model 3400, a J&W DB-5 fused silica capillary column and flame ionization detection. Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from PYR as a percentage of the moles of hydrogen required to form the most hydrogenated product, perhydropyrene. The hydrogenation products obtained from PYR were dihydropyrene (DHP) tetrahydropyrene (THF) and hexahydropyrene (HHP).

RESULTS AND DISCUSSION

In the liquefaction reactions performed in this research, two primary parameters were measured to evaluate the efficacy of the catalyst impregnation step. The first parameter was the conversion of Black Thunder coal to THF soluble material. The second parameter measured was the hydrogenation reactivity of the added aromatic, PYR, in the system. By determining the conversion of PYR to hydrogenated species and the percent hydrogenation to partially saturated products, the intrinsic activity of the catalyst added to the reaction system in a particular manner could be obtained. The only products observed from PYR were DHP, THP, and HHP. Usually, higher conversions resulted in the production of all three products. However, DHP was the primary hydrogenation product produced in all reactions. Both THP and HHP, when formed, were always minor products.

Reactions in 1-Methylnaphthalene. Liquefaction reactions performed in the nondonor solvent 1-MN using untreated and SO$_2$ treated Black Thunder coal are presented in Tables 1 and 2, respectively. Evaluation of the coal conversions obtained with the untreated (Table 1) or SO$_2$ treated coal (Table 2) indicated that the presence of a Mo or Ni based catalyst regardless of method of introduction increased coal conversion. The Molyvan L catalyst was more active for both coal conversion and PYR hydrogenation than was either Ni octoate or Mo naphthenate reacted without sulfur. Longer reaction times of 30 min resulted in higher coal and PYR conversions than did shorter reaction times of 20 min. The type of swelling solvent used made a difference in coal conversion, depending on the solvent used. Methanol appeared to be the most effective swelling solvent for Molyvan L while isopropanol was most effective for Ni octoate. Agitation of the swelling solvent with coal and catalyst present did not increase coal conversion. Doubling the catalyst loading and the amount impregnated into the coal yielded only a slight improvement in coal conversion but a more substantial improvement in PYR conversion. When the coal conversion of coal impregnated with catalyst during the swelling process was compared to that achieved when the catalyst was added directly to the reactor, the Molyvan L systems with THF and isopropanol swelling solvents yielded less conversion with impregnated catalyst while the systems with methanol yielded more. For Ni octoate, all of the impregnated coals yielded less conversion than the coal reacted with the catalyst in the slurry phase. Pyrene conversions were also higher when the catalyst was added directly to the reactor.

Reactions with SO$_2$ treated coal showed that swelling of the pretreated coal had less effect than swelling the untreated coal. Impregnation of Molyvan L with any of the three swelling solvents resulted in approximately 5% less coal conversion. Pyrene conversion remained high with Molyvan L; in some reactions adding the catalyst directly to the reactor yielded more activity while in other reactions the impregnated catalyst was more active. The type of swelling solvent had a stronger influence on coal conversion when Ni octoate was used as a catalyst. Higher coal and PYR conversions were achieved with Ni octoate when methanol was used as a swelling solvent than when either THF or isopropanol was used.

Reactions in V1074. A series of reactions was performed using THF as the swelling solvent and coal-derived V1074 as the reaction solvent (Table 3). Comparison of the reaction solvent V1074 to 1-MN for liquefaction of untreated Black Thunder coal showed a higher coal conversion with Molyvan L when no swelling prior to liquefaction was used. This advantage

of the coal-derived solvent was maintained when the coal was swelled prior to reaction and reacted without catalyst. However, when coal was swelled prior to liquefaction and Molyvan L was added either directly to the reactor or to the swelling solvent, the reaction solvent 1-MN yielded slightly higher coal conversion and nearly equivalent pyrene conversions. The coal and pyrene conversions were quite similar with Ni octoate in the two reaction solvents. With V1074, the highest coal conversion achieved occurred without prior swelling, followed by swelling with THF and adding the catalyst to the reactor; the least coal conversion was achieved when either catalyst was added to the THF swelling solvent. Substantial variability in coal and pyrene conversion occurred when Molyvan L was introduced into the swelling solvent indicating nonuniform absorption of the catalyst by the coal.

Reactions in Dihydroanthracene. Higher conversions of Black Thunder coal occurred in DHA when no catalyst was used. The hydrogen donor solvent promoted noncatalytic conversion of Black Thunder coal yielding 82.4% coal conversion after swelling in THF while 72.0% was achieved in V1074 and 59.7% in DHA. The highest coal conversion with Molyvan L in DHA was achieved without prior swelling, intermediate coal conversion occurred with swelling in THF and catalyst added directly to the reactor, while the lowest coal conversion occurred when the catalyst was added to the swelling solvent. The difference between the high and low values, though, was only 5%.

SUMMARY
The improvement in coal conversion expected by impregnating coal during the swelling process was not achieved. Swelling of untreated Black Thunder coal made the coal more accessible and more reactive under liquefaction conditions. However, absorbing the catalyst into coal, prior to liquefaction, thereby, making the catalyst more accessible to the dissolving coal molecule, did not achieve increased coal conversion at the liquefaction conditions used.

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Table 1. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: None				
None	0	NA[a]	NA	49.3±0.8	3.5±1.1	2.1±0.6
Molyvan L	709±39	NA	NA	82.4±3.0	30.0±5.4	11.2±2.4
Ni Octoate	604± 6	NA	NA	70.7±4.1	6.8±0.3	2.3±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	N[b]	34.2±7.0	59.7±8.9	0.0	0.0
Molyvan L	661±33	N	37.8±1.9	87.3±1.6	18.6±1.3	6.2±0.4
Ni Octoate	615± 6	N	41.3±0.6	77.0±0.1	2.4±0.1	1.2±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Mo Naphthenate	683	A	35.0±4.5	18.6±1.3	3.5±0.2	1.8±0.4
Molyvan L	544	N	40.4±1.8	81.9±1.6	15.1±1.8	5.7±0.4
Molyvan L	NM[c]	A	52.3±3.2	73.6±3.0	14.7±5.0	5.7±1.9
Molyvan L	1143	D	41.0±2.7	84.8±1.1	28.6±2.5	11.0±1.2
Ni Octoate	569	N	38.9±5.	74.8±12.9	11.1±11.0	4.7±4.1
Reaction Time: 20 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Mo Naphthenate	608±9.2	A	37.1±12.0	53.1±3.3	2.6±0.5	1.7±0.2
Molyvan L	NM	N	38.7±3.2	67.5±5.4	4.8±3.5	2.1±1.3
Ni Octoate	599	N	34.1±3.3	60.8±3.2	2.4±0.3	1.3±0.1

Table 1 (Continued)

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Reactor		
None	0	N	26.7±0.8	53.9±2.8	1.0±0.3	0.8±0.2
Molyvan L	690±19	N	18.6±0.6	88.0±0.9	24.3±1.8	8.5±1.1
Ni Octoate	698±70	N	18.6±0.6	85.5±0.1	10.9±0.4	4.0±0.4
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Swelling Solvent		
Molyvan L	644	N	25.2±4.9	68.4±0.0	3.0±0.8	1.7±0.5
Molyvan L	1261	D	26.2±3.4	88.8±0.5	25.7±2.7	9.9±1.3
Ni Octoate	653	N	23.3±0.8	70.1±1.1	3.5±0.4	1.9±0.1
Reaction Time: 20 min		Swelling Solvent: Methanol		Catalyst Added to Swelling Solvent		
Molyvan L	637	N	25.4±9.1	67.6±0.1	2.8±0.8	1.9±0.1
Ni Octoate	613±6.4	N	20.6±4.5	64.4±0.4	2.3±0.4	1.4±0.3
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to Reactor		
None	0	N	16.9±5.5	61.7±1.1	0.8±1.1	0.6±0.8
Molyvan L	623±37	N	17.9±6.9	88.1±0.4	18.7±0.8	6.6±0.3
Ni Octoate	658±1.4	N	16.3±3.8	77.6±1.1	2.2±0.4	1.1±0.1
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to the Swelling Solvent		
Molyvan L	645±26	N	18.2±1.1	79.9±0.8	16.9±2.3	6.5±0.8
Molyvan L	NM	D	22.8±1.5	81.9±1.8	28.2±0.4	10.9±0.3
Ni Octoate	667±70	N	15.6±3.7	75.2±0.8	3.9±0.6	1.9±0.3
Reaction Time: 20 min		Swelling Solvent: Isopropanol		Catalyst Added to the Swelling Solvent		
Molyvan L	572	N	18.6±0.6	68.2±4.0	4.5±1.8	1.9±0.7
Ni Octoate	699	N	15.6±3.7	64.8±3.7	4.3±0.4	2.2±0.1

[a]A = agitated: samples were agitated with catalyst for 96 hr; N = not agitated for 96 hr swelling period; D = catalyst level doubled. [b]NA = not applicable. [c]NM = not measured; catalyst loading should be between 550 and 750 ppm.

Table 2. Coal and Pyrene Conversions for SO_2 Treated Black Thunder Coal Reacted in 1-Methylnaphthalene

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: None				
None	0	NA[a]	NA	47.3±1.1	1.5±1.1	0.7±0.7
Molyvan L	623±12	NA	NA	88.5±0.7	27.8±3.0	10.4±0.6
Ni Octoate	696±143	NA	NA	76.3±4.2	12.5±3.5	4.2±1.2
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	N[b]	87.6±2.7	58.0±9.5	0.0±0.0	0.0±0.0
Molyvan L	683±53	NA	79.5±0.8	91.2±1.5	25.4±0.1	9.1±0.1
Ni Octoate	665±23	N	97.4±3.7	72.5±5.8	2.2±0.4	1.2±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Molyvan L	638	N	76.1±18.2	86.0±2.2	31.4±0.8	12.5±0.4
Ni Octoate	659	N	58.9±26.7	71.4±4.1	6.9±1.2	3.1±0.4
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Reactor		
None	0	N	38.4±2.3	41.8±2.4	1.5±0.1	1.0±0.0

Table 2. (Continued)

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Molyvan L	672±18	N	36.9±7.4	90.0±1.3	30.0±4.4	11.2±1.5
Ni Octoate	655±2.1	N	31.6±7.4	78.7±1.1	4.9±0.8	1.8±0.6
Reaction Time: 30 min		Swelling Solvent: Methanol		Catalyst Added to Swelling Solvent		
Molyvan L	NMᶜ	N	43.7±5.2	85.1±5.7	26.8±2.8	11.1±1.6
Ni Octoate	NM	N	33.4±4.8	78.4±0.2	7.1±0.5	3.1±0.1
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to Reactor		
None	0	N	45.0±0.0	56.4±3.0	1.6±0.1	1.1±0.1
Molyvan L	642±25	N	38.6±5.0	91.3±0.6	21.3±2.4	8.0±1.1
Ni Octoate	674±26	N	32.3±6.4	73.9±5.1	3.9±0.6	2.1±0.0
Reaction Time: 30 min		Swelling Solvent: Isopropanol		Catalyst Added to Swelling Solvent		
Molyvan L	NM	N	32.5±1.2	87.6±1.0	26.0±0.2	10.4±0.1
Ni Octoate	NM	N	25.0±0.0	67.9±2.3	5.0±0.2	2.4±0.0

ᵃNA = not applicable. ᵇN = not agitated during 96 hrs swelling period. ᶜNM = not measured.

Table 3. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in V1074

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation %
Reaction Time: 30 min		Swelling Solvent: None		Catalyst Added to Reactor		
Molyvan L	652±18	NAᵃ	NA	84.7±1.0	14.9±2.8	5.7±1.1
Ni Octoate	668±41	NA	NA	79.8±3.5	5.5±4.4	2.0±1.6
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	Nᵇ	25.0±3.3	72.0±1.7	5.3±0.1	3.0±0.1
Molyvan L	670±57	N	38.7±9.7	82.8±2.0	28.0±0.3	11.8±0.3
Ni Octoate	663±4.2	N	35.0±4.5	77.2±1.8	6.4±0.0	3.3±0.1
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Molyvan L	NMᶜ	N	38.3±1.1	76.0±8.1	14.1±2.3	6.1±0.8
Ni Octoate	NM	N	26.7±0.8	79.5±3.5	4.6±1.5	2.5±0.7

ᵃNA = not applicable. ᵇN = not agitated for 96 hr swelling period. ᶜNM = not measured; catalyst loading should be between 500 and 700 ppm.

Table 4. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in Dihydroanthracene

Catalyst Type	Catalyst Loading	Conditions During Swelling	% ΔV	Coal Conversion (mol %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		Swelling Solvent: None		Catalyst Added to Reactor		
Molyvan L	677±23	NAᵃ	NA	89.7±0.2	15.2±4.5	5.4±1.8
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Reactor		
None	0	Nᵇ	36.5±2.3	82.4±2.1	9.3±0.2	6.0±0.1
Molyvan L	658±33	N	22.2±0.7	87.3±2.8	23.5±4.7	9.4±1.8
Reaction Time: 30 min		Swelling Solvent: THF		Catalyst Added to Swelling Solvent		
Molyvan L	NMᶜ	N	41.0±6.4	84.5±0.4	8.9±2.3	4.6±0.8

ᵃNA = not applicable. ᵇN = not agitated for 96 hr swelling period. ᶜNM = not measured; catalyst loading should be between 500 and 700 ppm.

USING WATER AND DISPERSED MoS$_2$ CATALYST
FOR COAL CONVERSION INTO FUELS AND CHEMICALS

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Keywords: Water, Dispersed Mo Catalyst, Coal Liquefaction

INTRODUCTION

The historical development and advantages of dispersed catalysts for direct coal liquefaction have been reviewed by Weller [1982, 1994], and by Derbyshire [1988, 1990]. Due to their intimate contact with the surface of coal particles, the use of dispersed catalysts facilitates the activation and transfer of hydrogen to coal-derived radicals or reactive fragments in the early stage of coal conversion into soluble products. Recently it has been recognized that coals are more reactive than had been thought previously, especially low-rank coals. Laboratory research has clearly demonstrated that dispersed catalysts can have significant impact on coal liquefaction, even with the solid coal without solvent at temperatures as low as 325-350°C, as reflected by the increase in coal conversion [Bockrath et al., 1986; Derbyshire et al., 1986a, 1986b; Garcia and Schobert, 1989; Burgess and Schobert, 1991; Solomon et al., 1991; Song et al., 1986, 1991, 1993, 1994a; Huang et al., 1992, 1993]. Spectroscopic characterization of residues from liquefaction of Blind Canyon bituminous coal (at 350 or 400°C) using dispersed Mo and Fe catalysts (introduced onto coal by impregnation) has revealed that the metallic species have fully penetrated the coal particle [Anderson et al., 1993; Sommerfield et al., 1992, 1993]. Recent pilot plant tests have also demonstrated that the use of dispersed catalyst can be superior to supported catalyst for primary liquefaction (dissolution) of coal, particularly subbituminous coals [Vimalchand et al., 1992; Lee et al., 1992; Swanson, 1992a, 1992b]. Coal-derived liquids can be used as sources of aromatic chemicals and polymeric materials as well as transportation fuels [Song and Schobert, 1993; Derbyshire et al., 1994].

This paper reports on an alternative process for converting coal to liquid fuels and useful chemicals through low-severity liquefaction using dispersed MoS$_2$ catalyst with added water. It is well known that water or steam deactivate hydrotreating catalysts, such as Mo-based catalysts, under conventional process conditions. For coal liquefaction using dispersed catalysts, drying after impregnation of catalyst or precursor salt has been a standard procedure [Weller and Pelipetz, 1951; Derbyshire et al., 1986a, 1986b; Garcia and Schobert, 1989; Artok et al., 1993; Weller, 1994]. It was demonstrated that water removal and the drying conditions after impregnation of catalyst precursor were influential for liquefaction of subbituminous and bituminous coals at 400°C [Derbyshire et al., 1986b]. Several groups have reported on the negative impacts of water addition in catalytic coal liquefaction [Bockrath et al., 1986; Ruether et al., 1987; Kamiya et al., 1988]. In a preliminary work, however, we have observed the synergistic effect between water and dispersed molybdenum sulfide catalyst for promoting coal liquefaction at a temperature (350°C) lower than those used in the previous studies mentioned above [Song et al., 1993]. The motivation of our study comes from several interesting findings in our recent work on the influence of drying (water removal) and oxidation of Wyodak subbituminous coal on its catalytic liquefaction at 350°C [Song et al., 1994a].

EXPERIMENTAL

The coal used was a Wyodak subbituminous coal, which is one of the Department of Energy Coal Samples (DECS-8) maintained in the DOE/Penn State Sample Bank. Detailed properties of the coal are described elsewhere [Song et al., 1994a]. Ammonium tetrathiomolybdate (ATTM) was dispersed as a catalyst precursor on to coal (1 wt% Mo on dmmf basis) by incipient wetness impregnation from its aqueous solution. ATTM is expected to generate molybdenum sulfide particles on coal surface upon thermal decomposition at ≥ 325 °C [Garcia and Schobert, 1989; Artok et al., 1993]. The impregnated or the raw coal samples were dried in a vacuum oven at 100 °C for 2 h before use. For the experiments with added water, the weight ratio of water to dmmf coal was kept at 0.46.

The liquefaction was carried out in 25 mL tubing bomb reactors at a given temperature (350, 375, 400, 425°C) for 30 min (plus 3 min heat up) under an initial H$_2$ pressure of 6.9 MPa. For the experiments with added water, the weight ratio of added water to dmmf coal was kept constant (0.46) for both thermal and catalytic runs. All the liquefaction reactions described here were carried out in the absence of any organic solvents. The yields of gaseous products were determined in two different ways: by weight difference of microreactor (method I) and by GC analysis (method II). More experimental details have been given elsewhere [Song et al., 1993].

The oils were analyzed using a Waters high-performance (high-pressure) liquid chromatography (HPLC) equipped with a photodiode array (PDA) detector and Millennium 2010 Chormatography-Manager software system, which allows continuous two-dimensional scanning analysis over UV/VIS range. The molecular components in oils were identified using gas chromatography combined with mass spectrometry (GC-MS). More analytical details may be found elsewhere on the two-dimensional HPLC [Saini and Song, 1994] and GC-MS [Song et al., 1994b].

RESULTS AND DISCUSSION

Liquefaction at 350°C

Figure 1 shows the effect of water addition on the liquefaction of Wyodak subbituminous coal at 350°C for 30 min in the absence of a organic solvent. Relative to the non-catalytic run of vacuum-dried coal, the addition of water improved coal conversion from 14.5 to 22.5 wt% (dmmf). The use of ATTM increased the coal conversion from 14.5 to 29.8 wt%. On a percentage basis, the use of ATTM and the addition of water improved coal conversion by 106% [(29.8-14.5)/14.5=1.06] and 55%, respectively, as compared to the non-catalytic run of the vacuum-dried coal. Adding a small amount of water to the catalytic reactions at 350°C dramatically increased coal conversion, to 66.5 wt%. This represents a 123% increase from the catalytic run without water, and 359% increase from the non-catalytic run without water. We have confirmed these trends by duplicate experiments. These interesting findings indicate that dispersed molybdenum sulfide catalyst and added water can act in concert to promote coal liquefaction at relatively low temperature, 350°C.

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Figure 2 indicates that the addition of water caused substantial increase in gas yields. This is manifested primarily by the increased CO_2 yield. CO yield decreased upon water addition, indicating the occurrence of water-gas-shift (WGS) reaction (eq. 1). According to the WGS reaction, the increased amount of CO_2 is 1.57 times the decreased amount of CO (MW ratio: 44/28 = 1.57). However, when water is added to the non-catalytic reaction of vacuum-dried coal, CO_2 yield increased from 4.5 to 8.3 wt% on a dmmf basis, whereas the CO yield decreased from 0.24 to 0.12 wt% (dmmf). A similar trend was observed in catalytic runs at 350°C (Figure 2). Apparently, the enhanced CO_2 formation is due primarily to the addition of water, but not the WGS reaction. Probably the majority of increased CO_2 yield is due to chemical reactions between the water and the species in coal or coal products, such as the reaction between water and carbonyl groups, as shown by eq. 2. This could partially rationalize the enhanced CO_2 formation together with increased coal conversion upon water addition.

$$CO + H_2O = CO_2 + H_2 \qquad\qquad 1)$$
$$RCOR' + H_2O = RH + CO_2 + R'H \qquad\qquad 2)$$
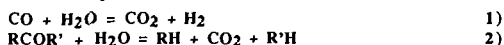
Effect of Reaction Temperature in the Range of 325-425°C
Figure 3 shows the effect of water on the thermal and catalytic liquefaction at 400°C for 30 min. Compared to the runs at 350°C, the positive effect of water addition to the non-catalytic run becomes much less, but the positive impact of using ATTM becomes much more remarkable. The use of ATTM for reaction at 400°C for 30 min afforded a high coal conversion, 85.4 wt% (dmmf), and a high oil yield, 45.8 wt%. However, addition of water to the catalytic run decreased coal conversion (to 62.1 wt%) and oil yield (to 28.2 wt%). This is in distinct contrast to the trends for corresponding runs at 350°C. We have performed several tests and have confirmed this trend. An important implication from Figure 3 is that the presence of water in the catalytic run at 400°C decreased the catalytic activity level that can be achieved in the absence of water. In other words, water tends to passivate the dispersed catalyst at higher reaction temperatures (400, 30 min).

It is clear from Figures 1 and 3 that water can affect coal conversion in opposite directions at different temperatures. Therefore, we further examined the effect of reaction temperature in the range of 325-425°C at 25°C interval. Figure 4 shows the coal conversion as a function of reaction temperature for catalytic liquefaction using ATTM precursor with added water. It appears that coal conversion displays a volcano-shape change with increasing temperature from 325°C to 425 °C. Coal conversion increased with temperature up to 375°C and decreased with further increase in temperature up to 425°C. At 375°C, maximum coal conversion, nearly 80 wt%, was achieved with added water in solvent-free catalytic runs. This suggests that retrogressive reactions in the coal-H$_2$0-catalyst system become considerable at higher temperatures (400-425°C).

HPLC and GC-MS Analysis of Oils
We have reported on the characterization of oils using two-dimensional HPLC and GC-MS techniques in a companion paper [Saini and Song, 1994]. In the present work we also applied these techniques. Figures 5 and 6 show the three-dimensional HPLC chromatograms of oils from water-assisted liquefaction at 350°C with and without the catalyst, respectively. In these 3-D chromatograms, peak intensity is plotted against UV wavelength range (250-400 nm) and retention time (0-120 min). The peaks between 2-30 min are due to 1-, 2-, 3- and 4-ring aromatics, and the two peaks between 50 and 60 min are due to phenolic compounds. Comparison of Figure 6 with Figure 5 indicates that the oils from liquefaction with added water contain more phenolic compounds. We also confirmed this trend by GC-MS analysis. It should be noted that the phenolic compounds as well as alkylaromatics in the oils may be industrially useful chemical feedstocks [Song and Schobert, 1993].

Role of Water in Thermal and Catalytic Reactions
Our results show that, at constant water/coal ratio (0.46, wt ratio), water can have either a strong promoting effect or an inhibiting effect on coal conversion in catalytic liquefaction, depending on the reaction conditions. The most interesting finding from our work is the strong synergistic effects between water and dispersed molybdenum sulfide catalyst under certain conditions. This finding is important both from fundamental and practical viewpoints. Little has been reported in the literature on the positive effect of water addition on catalytic liquefaction under H$_2$ pressure. The results of Bockrath et al. [1986] showed that using water (water/coal = 2, wt ratio) as solvent in the catalytic liquefaction of Illinois No.6 coal at 350°C for 60 min gives much lower conversions than the runs using organic solvents. In an earlier work, Ruether et al. [1987] examined the effect of water addition in catalytic liquefaction of Illinois No.6 coal at 427°C for 1 h (water/coal = 0.33-1.5, wt ratio). They concluded that "at fixed total pressure, the most reactive environment contains no added water, so that H$_2$ partial pressure is as high as possible". In the runs using 0.1% dispersed Mo catalyst at 427 °C for 60 min, highest coal conversions were obtained without added water. They reported that "the absence of any positive effect of water in catalyzed reaction systems could be explained on the basis of a very strong catalytic effect of molybdenum in promoting hydrocracking and hydrogenation reactions." Kamiya et al. [1988] have observed that addition of water deactivates the iron catalyst for liquefaction of a brown coal at 400°C for 30 min and for upgrading of SRC from Wandoan coal (water/SRC = 0.1-0.2 wt ratio) at 450°C for 60 min. The negative influence of water was thought to arise from reoxidation of the active iron sulfide catalyst. Consequently, addition of sulfur can resist reoxidation of iron catalyst by water under coal liquefaction conditions [Kamiya et al., 1988]. Mikita et al. (1988) reported on using water and non-donor vehicles for liquefaction of Illinois No.6 coal at 385°C for 30 min. Their work was directed toward replacing or reducing the amount of organic recycle vehicle. They observed that coal conversion in water is greater than with dry hydrogenation under otherwise comaprable conditions. Conversion in a non-catalytic run with SRC II solvent and a small amount of water (water/coal=1.7 g/4 g) was similar to a catalytic run with 0.1 wt% Mo and a larger amount of water (water/coal=3.4 g/4 g) (86-88 wt% vs 86-90 wt%). From these results they concluded that in the presence of Mo catalyst and water, it is not necessary to use hydrogen donor solvent. As discussed above, we have not found any published literature that reports on strong synergistic effect between water and dispersed catalyst for coal liquefaction.

The strong promoting effect of water on catalytic liquefaction at 325-375°C observed in our work may be partially understood by the literature information from non-catalytic reactions. The orgin of the above-mentioned strong synergism, however, has not been clarified. For non-catalytic coal conversion such as pyrolysis, liquefaction and coprocessing, hydrothermal pretreatments of coal has been reported to be beneficial in terms of increased conversion, or oil yield [Graff and Brandes, 1987; Bienkowski et al., 1987; Ross and Hirschon, 1990; Pollack et al., 1991; Serio et al., 1991, 1992a, 1992b; Tse et al., 1991]. Lewan [1992] suggested that water could act as a source of hydrogen and oxygen in petroleum formation by hydrous pyrolysis. Siskin et al. [1991] have suggested that the presence of water during coal pretreatment will facilitate depolymerization of the macromolecular structure to give an increased proportion of liquids by cleaving important thermally stable covalent cross-links in the coal structure. On the other

hand, Tse et al. [1991] suggested that the pretreatments of low rank coals in the presence of water should minimize retrogressive reactions such as crosslink formation from phenolics and lead to higher conversion or a better quality product.

SUMMARY

We have found that there are strong synergistic effects between water and a dispersed molybdenum sulfide catalyst for promoting low-severity liquefaction of Wyodak subbituminous coal. There is substantial improvement in coal conversion upon addition of water to the reaction using dispersed Mo catalyst at relatively low temperatures, 325-375°C. Relative to the non-catalytic run of the dried coal, the co-use of the catalyst and water (at water/dmmf coal = 0.46) can double the coal conversion at 350°C for 30 min, from 29-30 to 66-67 wt%. On the other hand, water tends to passivate the dispersed catalyst at higher reaction temperatures (400-425°C, 30 min). HPLC and GC-MS of oils revealed that the oils from liquefaction with added water contain more phenolic compounds. However, some fundamental questions concerning the role of water in catalytic liquefaction and catalytic reaction mechanisms involving water need to be answered by further research.

ACKNOWLEDGMENTS

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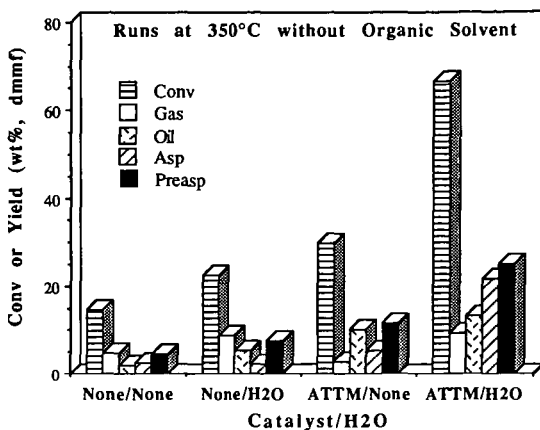
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Figure 1. Effect of water on catalytic liquefaction of Wyodak coal at 350°C for 30 min.
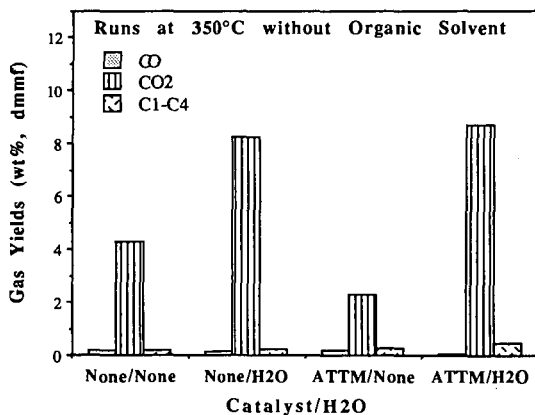

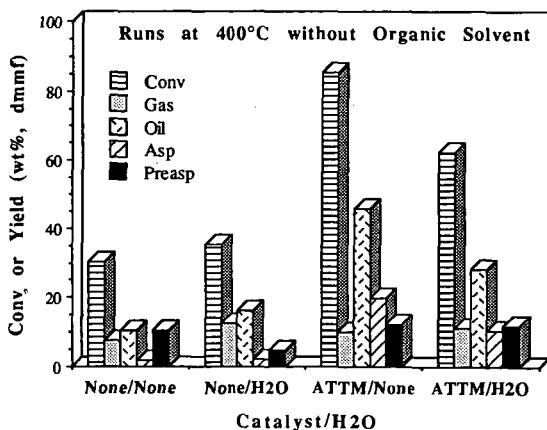**Figure 2.** Effect of water on gas formation in catalytic liquefaction at 350°C for 30 min.

Figure 3. Effect of water on catalytic liquefaction of Wyodak coal at 400°C for 30 min.
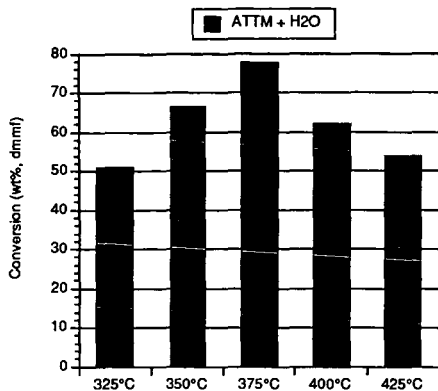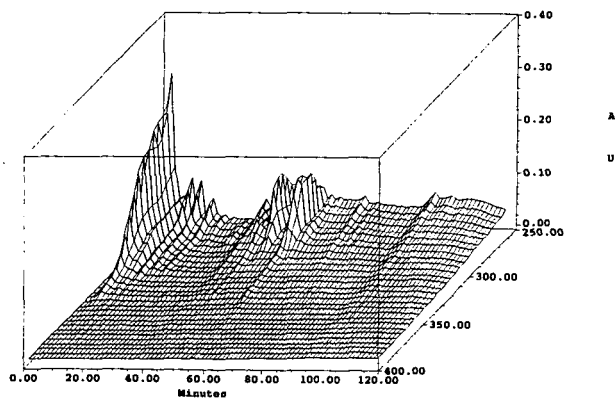
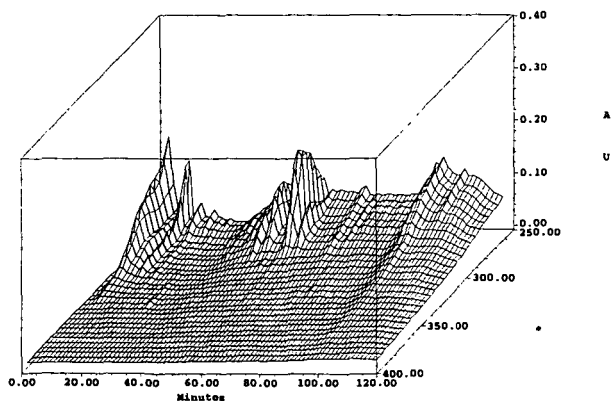**Figure 4.** Effect of temperature on conversion of Wyodak coal in the presence of H_2O without any organic solvent

Figures 5. 3-D HPLC chromatogram of oils from non-catalytic liquefaction of Wyodak coal at 350°C for 30 min in the presence of water.

Figures 6. 3-D HPLC chromatogram of oils from catalytic liquefaction of Wyodak coal at 350°C for 30 min with dispersed Mo catalyst in the presence of water.

CATALYST PERFORMANCE IN ASHY-RESID CONTAINING RECYCLE OILS

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Keywords: Coal liquefaction, catalyst, iron, molybdenum

INTRODUCTION

In recent years, the objective for coal liquefaction has switched from producing primarily a resid to making exclusively distillate product. In this revised configuration, improving conversion of the residual fraction becomes essential for developing a viable process.[1] Since resid conversion under typical process conditions does not proceed to any significant extent in the absence of a catalyst,[2,3] developing improved catalysts is a key element for improving the process. Although there is continuing interest in developing catalysts for coal liquefaction,[4] much of this research effort has not been specifically directed toward conversion of coal in media incorporating coal-derived resid.[5] The criteria for optimizing resid conversion is to maximize distillate yields at low hydrogen consumption levels while limiting gas make.[6] Therefore, viable catalysts must be capable of meeting these criteria for resid conversion as well as attain maximum dissolution of the coal.

Both particulate and highly dispersed catalysts have been used for converting residual feeds to distillate products.[7] At the Advanced Coal Liquefaction Research and Development Facility at Wilsonville, Alabama, in thermal/catalytic or catalytic/thermal Runs 260, 262 and 263, an organically dispersed molybdenum catalyst (Molyvan L) plus iron oxide was used along with a particulate nickel-molydenum catalyst.[8] This system of dispersed iron and molybdenum catalysts along with a supported particulate catalyst gave higher yields of C_4^+ distillate than either system alone and among the highest ever observed. To realistically evaluate catalysts for processing resid containing feedstocks, it is necessary to measure their activity in feeds containing significant concentrations of residual material. This paper presents the results of a study in which catalyst candidates were evaluated in resid containing process solvents that were obtained from Wilsonville.

EXPERIMENTAL

Wyodak coal obtained from the Black Thunder Mine in Wright, Wyoming, was ground to -200 mesh, riffled and stored under nitrogen at 4 °C. This material was supplied by CONSOL Inc. Proximate and ultimate analyses of the coal are presented in Table 1. A sample of V-131B recycle oil from Run 258 was obtained from Wilsonville. Samples of the individual components that were combined into the Run 262 recycle oil were obtained from CONSOL Inc. These included the V-1074 heavy distillate from the vacuum tower, the V-130 deashed resid product from the ROSE-SR deashing unit, and the V-1082 ashy resid feed to the deashing unit. All of these materials were produced at Wilsonville when the plant was operating in a close-coupled configuration and feeding Black Thunder coal. Analyses of these recycle oils given in Table 2 show that both contain sizable concentrations of iron resulting from addition of iron oxide to the feed slurries. Run 262 process oil also contains a sizable concentration of Mo since Molyvan L, an organic-based Mo containing material, was being added during this run. Based on previous Mössbauer studies on similar material, the iron is present in combination with sulfur as pyrrhotite. The molybdenum was presumed to be present as MoS_2. Each of the recycle oils was characterized by separating into tetrahydrofuran (THF) insoluble, THF soluble-pentane insoluble, and pentane soluble fractions (see Table 2). A sample of THF insoluble material in the Run 262 V-1082 ashy resid was isolated by exhaustively extracting with THF for 2 days and drying overnight at 40 °C at 125 torr. A sample of the iron oxide catalyst (IO) that had been used at Wilsonville was supplied by CONSOL Inc. Molyvan L was supplied by R. I. Vanderbilt Co. A sample of superfine iron oxide (SFIO), which was described previously, was supplied by Mach I Company, King of Prussia, Pa.[9] Impregnated coals were prepared as previously described.[10]

Reactions were conducted in 50 cc microautoclaves pressurized to 1000 psig hydrogen at ambient temperature. In coal reaction experiments, 5.4 g of solvent, 3 g of coal, catalyst and dimethyl disulfide were added to the reactor. After pressurization, the reactor was placed in a fluidized sandbath set at the specified temperature and continuously agitated at a rate of 400 cycles per minute. At the end of the reaction period, the reactor was quenched to ambient temperature and the gaseous products collected and analyzed by gas chromatography. The solid and liquid products were scraped from the reactor using THF and the mixture was extracted in a Soxhlet apparatus for 18 hours. The THF insoluble material, which included IOM and ash, was dried (80 °C at 125 torr) and weighed. The THF solubles were concentrated by removing excess THF in a rotary evaporator and subjected to either a solvent separation scheme, which was described previously,[9] or vacuum distillation using a modified D-1160 procedure, which is described elsewhere.[11] The methods for calculating material balances are

included in the previous descriptions. In the following discussion, coal conversion equals 100 minus the yield of THF-insoluble organic material (IOM).

Reactivity of Residual Feeds

Samples of Wilsonville produced recycle oils or their individual components were used for evaluating catalysts. These oils contained slightly more than 40 wt% 1050 °F heavy distillate and 30-35 wt% resid, as shown in Table 2. The combined mineral matter and IOM made up the remaining 25-30 wt% of this material, nearly equivalent to the feed coal used at Wilsonville in these runs. The higher oil and lower IOM concentrations in the Run 262 recycle oil, relative to the Run 258 recycle oil, indicates the higher level of conversion obtained in the presence of the added Mo catalyst. Each of the components in the Run 262 recycle oil were also subjected to solvent separation, the sum of which agreed with results from solvent separation of the combined Run 262 recycle oil. The Run 258 recycle oil was used as received.

The composition of the Run 262 recycle oil changes quite significantly at temperatures above 300 °C. As shown in Table 3, at 415 °C, the IOM in these recycle oils decreased from 14.0 wt% to 10.8 wt% after 30 min at 6.89 MPa H_2 (cold). A net conversion of both PA+A and IOM to pentane soluble oils occurred, both of which had been observed previously.[12,2] Formation of hydrocarbon gases and $CO+CO_2$ was minimal. In a series of similar runs at 415 °C ranging from 3.8 min to 60 min, the THF-IOM concentration decreased rapidly from 14.0 wt% in the starting material to approximately 10 to 11 wt%, even at the shortest time (Table 4). This same level of reactivity was observed at 300 °C, both in the presence and absence of hydrogen overpressure. The product from this latter run indicated a somewhat smaller shift to oil product. Similar reactivity was observed in the ashy resid fraction in the absence of any distillate solvent. The IOM decreased from an initial 26.8 wt% in the starting ashy resid to 20.5 wt% after 15 min at 415 °C in 6.89 MPa H_2 (cold). This corresponded to 24 wt% conversion of the IOM. Therefore, most of the reaction is occurring in the residual fraction in the absence of donor solvent and independent of the presence of gaseous hydrogen, which appears to have a slightly positive effect. A sample of IOM that had been isolated from the ashy resid was subjected to reaction in tetralin at 415 °C for 15 min with 6.89 MPa H_2 (cold). Because only 5.2 wt% was solubilized, it appears this material does not respond to normal liquefaction conditions.

This change in ashy resid solubility in THF may be due to disassociation of the material making it more soluble in THF. Earlier results on vacuum tower bottoms and ROSE-SR ash concentrate showed that pyridine and mixed cresylic acids were significantly better solvents than THF.[13] However, a comparison of the insoluble organic matter in the Wilsonville filter feed stream determined with each of these solvents showed that pyridine, quinoline and mixed cresylic acids gave essentially the same result.[14] In our laboratory, we determined the solubility of ashy resid in pyridine, THF and cresylic acids using a Soxhlet technique for pyridine and THF and the Wilsonville procedure for cresylic acid.[15] The insolubles in THF, pyridine and cresylic acids were 26.8, 23.1 and 24.0 wt%, respectively. In refluxing pyridine at 114 °C, as compared to the 84 °C temperature attained when using the Soxhlet, the insolubles decreased further to 21.4 wt%, which was very close to the 20.5 wt% THF IOM obtained after reacting the ashy resid at 415 °C for 15 min in 6.89 MPa H_2 (cold).

The reactivity of the distillate fraction further complicated use of these materials in evaluating catalyst performance. The THF IOM fraction of this material was 3.1 wt% of which 1.8 wt% remained insoluble after heating at 300 °C in hydrogen for 15 minutes. This amount, though relatively small on a percentage basis, makes a larger impact on the amount of IOM in the sample that is converted and affects the overall conversion numbers.

Reactivity of Coal in Recycle Oil

The conversion and product yields of Black Thunder Wyodak coal were determined using these Wilsonville derived recycle oils. Both oils contained sizable amounts of iron while the Run 262 oil also contained 163 ppmw molybdenum. For a 30 wt% coal concentration in the feed, this corresponds to a 300 ppmw Mo concentration on moisture and ash-free coal. Various iron and iron-molybdenum catalysts were added to these reaction systems; iron up to 1.0 wt% and Mo up to 1000 ppmw, based on maf coal, were added as shown in Table 5. Reactions were run at 440 °C for 22 min after which they were analyzed either by solvent separation or vacuum distillation. The amount of conversion was, of course, influenced by the IOM present in the starting recycle oil that became solubilized, which explains the >100% values. Vacuum distillation was also used to measure the amount of conversion to distillable oils. A corresponding THF conversion value was also obtained using this technique since THF insolubles were removed prior to distillation.

Although there is considerable scatter in the data, it is clear that as Mo concentration increases, reactivity improves. In Figure 1 THF conversion increases quite sharply from a low of 96 wt % in the

absence of Mo. Similarly, C_5 solubles also increase as shown in Figure 2. This value increases from a low of 32 wt% in the absence of Mo up to 59 wt% upon addition of 1000 ppmw Mo. The corresponding 1050 °F value also varies similarly but with somewhat more scatter, as shown in Figure 3. These data indicate that distillate yield levels out at a Mo addition level of about 500 ppmw for the Run 258 recycle oil. All of the distillate yields taken in Run 262 recycle oil that already contained recycled Mo, were at a maximum, indicating that recycle oil performance had been optimized in Run 262.

The most striking example that fails to fall within this pattern is the reaction in the presence of SFIO to which no Mo had been added. Of the 2.9 wt% Fe present in the reaction feed, only 0.8 wt% was SFIO. Surprisingly, its THF conversion, C_5 solubles and 1050 °F distillate yield appears to be equivalent to addition of approximately 500 ppmw Mo in the Run 258 recycle oil. These data support a significant activity for this nanometer size material.

Conclusions
The assessment of the activity of fresh catalysts for liquefaction of Wyodak coals in Wilsonville recycle oils is complicated by the presence of resid, unconverted coal, ash and dispersed catalyst. The presence of a THF-insoluble fraction that easily converts at temperatures above 300 °F in an inert atmosphere to a THF-soluble fraction results in apparent conversions of coal in excess of 100%, even under the mildest of conditions. Solubilization of this material was observed in refluxing pyridine at 114 °C, as well as this material is not susceptible to reaction in tetralin and hydrogen at reaction conditions to form a THF soluble material. Addition of Mo to Mo-free recycle oils resulted in increased THF-conversion, pentane solubles yield, and 1050 °F$^+$ conversion. Accumulated Mo catalyst in recycle oils, taken from runs at Wilsonville where dispersed Mo was being added, masks the effect of added fresh Fe or Mo catalysts. Catalyst testing in these systems requires careful control of the components in the residual fraction.

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Table 1. Black Thunder Coal Analysis					
Proximate Analysis	wt%	Ultimate Analysis	wt%	Sulfur Types	wt%
Moisture	21.2	Carbon	68.68	Total	0.39
Ash	5.15	Hydrogen	4.76	Pyritic	0.07
Volatile Matter	34.4	Nitrogen	1.21	Sulfate	0.09
Fixed Carbon	39.3	Sulfur	0.56	Organic	0.23
		Oxygen (diff)	18.25		
		Ash	6.54		
		Ash, SO_3-free	5.42		

Table 2. Recycle Oil Characterization, wt%		
	Run 262 V-131B[a]	Run 258 V-131B
1050°F Distillate	44.2	46.6
Ash	8.3	8.1
THF IOM	12.8	15.1
PA+A	18.6	22.1
Oils	60.3	54.7
Iron	1.7	1.2
Molybdenum, ppmw	163	3

a. Prepared by blending V-1074 heavy distillate, V-130 deashed resid and V-1082 ashy resid in ratio 42.7:6.6:50.7, respectively.
b. Not available

Table 3. Reaction of Run 262 Recycle Oil[a]			
wt% af WRO	Reactants	415°C for 30 min	300 °C for 15 min
HC Gases	0.0	0.1	-
CO+CO_2	0.0	0.1	-
Oils	65.7	71.2	69.5
PA+A	20.3	17.8	19.6
IOM	14.0	10.8	11.0
IOM Conversion	-	23	21

a. No coal, 5.4 g Run 262 recycle oil, 6.89 MPa H_2 cold.

Table 4. Disappearance of IOM from Run 262 Recycle Oil[a]			
Temperature, °C	Gas[b]	Time, min	THF IOM[c]
415	H_2	0	14.0
415	H_2	3.8	11.3
415	H_2	7.5	11.1
415	H_2	15	10.9
415	H_2	30	10.8
415	H_2	60	10.1
300	H_2	15	11.0
300	N_2	15	11.7

a. Recycle oil contains 1.8 wt% Fe on ash-free basis.
b. Pressure 6.89 MPa (cold).
c. Weight percent ash-free solvent on SO_3-free ash basis.

No.	Recycle Oil Wilsonville Run No.	Form of Catalyst	Added Catalyst[a]			
			Fe, wt%	Fe carrier	Mo, ppmw	Mo Carrier
1	258	none	-	-	-	-
2	258	Particulate	1	IO	100	MVL
3	258	Impregnated	0.78	FOH	-	-
4	258	Impregnated	0.8	FeIII	-	-
5	258	Particulate	0.8	SFIO	-	-
6	258	Impregnated	0.8	FeIII	250	AM
7	258	Impregnated	0.8	FeIII	500	AM
8	262	Impregnated	0.8	FeIII	550[b]	AM
9	262	Impregnated	0.8	FeIII	800[b]	AM
10	258	Impregnated	0.8	FeIII	1000	AM

Table 5. Figure Legend

a. IO = iron oxide from Wilsonville; MVL = Molyvan L; FOH = FeOOH formed by base precipitation of ferric nitrate; SFIO = superfine iron oxide; AM = ammonium molybdate impregnated on coal as aqueous solution; FeIII = $Fe_2(SO_4)_3 \cdot 5H_2O$ impregnated on coal as aqueous solution.
b. Includes Mo in recycle oil, 300 ppmw on maf coal.
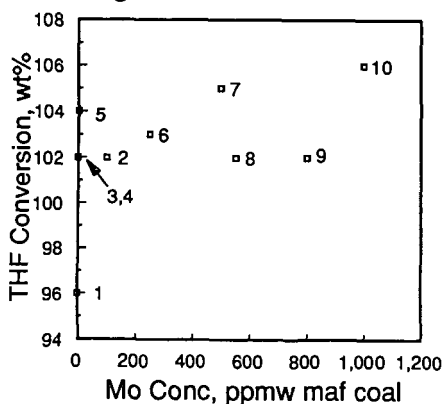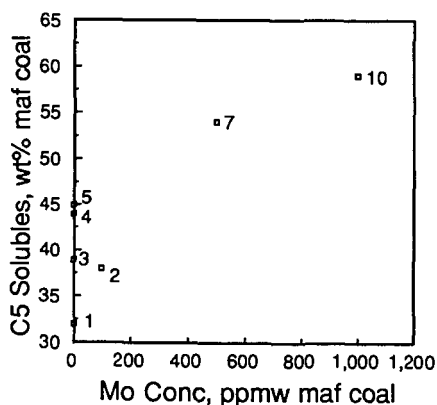

Figure 1. THF Conversion

Figure 2. Pentane Soluble Oil

Figure 3. Distillate Oil Yield